

## Content, association and modes of occurrence of mercury in biomass ashes and its behaviour during biomass combustion

Stanislav V. Vassilev<sup>1\*</sup>, Christina G. Vassileva<sup>1</sup>, Mariya G. Georgieva<sup>1</sup>,  
Gergana G. Velyanova<sup>1</sup>, Lora S. Bidzhova<sup>2</sup>, Svetoslav V. Georgiev<sup>2</sup>

<sup>1</sup> Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 107, Sofia 1113, Bulgaria; e-mails: vassilev\_stan@yahoo.com (\*corresponding author); ch\_vassileva@yahoo.com; mgeorgieva@imc.bas.bg; gergana315@gmail.com

<sup>2</sup> Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 24, Sofia 1113, Bulgaria; e-mails: lora.bidzhova@gmail.com; s\_georgiev@geology.bas.bg

(Received: 30 January 2025; accepted in revised form: 20 March 2025)

**Abstract.** Toxic Hg species pose a global ecological threat due to the significant anthropogenic emissions of Hg to the atmosphere, particularly during coal combustion. An investigation about the content, association and modes of occurrence of Hg in diverse biomass ash (BA) varieties and its behaviour during biomass combustion was performed. These BAs belonging to woody, herbaceous, agricultural and aquatic biomass groups were examined with different chemical and mineralogical methods, as well as thermal and leaching procedures. The Hg contents in BAs are low and vary between 0.0032 and 0.0452 ppm (mean 0.0225 ppm). About 60–99% (mean 87%) and 63–100% (mean 91%) of Hg in biomass were volatilized at 500 °C and 700 °C, respectively, and only limited amounts of Hg were captured by BAs enriched mostly in salts such as carbonates, oxyhydroxides, phosphates, sulphates, and chlorides. The affinity of residual Hg in the BA system is towards relatively stable Fe-, P-, Ti- Al-, K-, and Si-bearing minerals (especially K aluminosilicates and Fe oxides), as well as less stable chlorides (particularly sylvite). The potential mode of Hg occurrence in BA is likely in the form of impurities in the above minerals. Alternative renewable fuels poor in Hg such as appropriate sustainable biomasses (0.001–0.043 ppm Hg) are suggested to partially or completely substitute the industrial coals enriched in Hg (0.14–0.57 ppm) and used in Bulgarian thermoelectric power plants and thus minimize the ecological problems related to this element.

Vassilev, S., Vassileva, C., Georgieva, M., Velyanova, G., Bidzhova, L., Georgiev, S. 2025. Content, association and modes of occurrence of mercury in biomass ashes and its behaviour during biomass combustion. *Geologica Balcanica* 54 (1), 17–35.

**Keywords:** Mercury, biomass ash, content, behaviour, association.

### INTRODUCTION

Mercury is a highly toxic element posing global ecological concern. Various highly volatile Hg species are easily transported at long distances and persistently bioaccumulated, having harmful impacts on the environment and causing acute toxicity and mutagenic effects in humans (Ishag *et al.*, 2022). The global Hg emissions to the atmosphere have

been estimated at approximately 7527 t per year, of which about 5207 t come from natural sources and around 2320 t are from anthropogenic sources (Pirrone *et al.*, 2010). A more recent summary estimates that the worldwide annual natural emissions and re-emissions are between 3995 t and 8600 t, whereas the annual global anthropogenic emissions are about 1870 t (Gworek *et al.*, 2020). Thus, many governments have proposed regulations to reduce

the impact of anthropogenic Hg emissions. On the other hand, Hg still has numerous applications in various industrial sectors, with an annual global Hg consumption of about 3798 t (Pacyna *et al.*, 2010). A number of comprehensive reviews and investigations discuss diverse issues related to Hg such as sources, Earth geobiochemical cycle, and pollution of vegetation, water, air, and soil, as well as the applications of different approaches for removal of Hg from fuels and reduction of Hg emissions during fuel combustion (Pacyna *et al.*, 2010; Pirrone *et al.*, 2010; Fitzgerald and Lamborg, 2014; Ariya *et al.*, 2015; Raj and Maiti, 2019; Zhao *et al.*, 2019; Charvát *et al.*, 2020; Gworek *et al.*, 2020; Grace Pavithra *et al.*, 2023; Wu *et al.*, 2024, among others). These studies show that there are still many uncertainties about the occurrence, behaviour and fate of Hg in natural and anthropogenic systems.

Mercury is one of the most studied trace elements in traditional solid fuels such as coal, municipal solid waste, and refuse-derived fuel, and occasionally petroleum coke, peat, and biomass. The worldwide average contents (the Clarke values) of Hg in plants, coals, peats, ashes, rocks, soils, waters, and other objects are provided in Table 1. It can be seen that the Hg values for coals, plants and their ashes are among the most enriched in this element compared with other objects. This heavy metal has low melting ( $-39\text{ }^{\circ}\text{C}$ ) and boiling ( $357\text{ }^{\circ}\text{C}$ ) points and high vapour pressure even at ambient temperatures. As a result, Hg reveals a high volatilization behaviour (83–100%) during coal and biomass combustion (Cohen and Dunn, 2004; Yudovich and Ketris, 2005b; Thy and Jenkins, 2010; Dziok *et al.*, 2020). For example, it is estimated that about 50–60% of Hg entering thermoelectric power plants (TPPs) worldwide is emitted into the atmosphere (Lopez-Anton *et al.*, 2009; Raj and Maiti, 2019). The dominant Hg species in the atmosphere are elemental Hg<sup>0</sup> (95% of the atmospheric Hg) and, to a lesser extent, oxidized Hg<sup>2+</sup> and particulate Hg (Ericksen *et al.*, 2003; Friedli *et al.*, 2003; Yudovich and Ketris, 2005a; Lopez-Anton *et al.*, 2009; Huang *et al.*, 2011; Zhao *et al.*, 2019; Charvát *et al.*, 2020). Consequently, a transboundary pollution of air, water, soil, and vegetation occurs through dry or wet deposition.

Coal combustion is the primary source of global anthropogenic Hg emissions to the atmosphere (Pirrone *et al.*, 2010; Zhao *et al.*, 2019; Charvát *et al.*, 2020) and contributes about 26% of the total Hg emissions (Raj and Maiti, 2019). The high Hg volatilization during coal combustion is caused by the occurrence of this sulphophile trace element

predominantly in unstable coal constituents such as organic matter, sulphides, native elemental Hg<sup>0</sup>, sulfosalts, selenides, chlorides, and sulphates, and occasionally oxides, silicates, carbonates, and gold (Yudovich and Ketris, 2005a, c; Kolker *et al.*, 2006; Hower *et al.*, 2010; Shah *et al.*, 2010; Ariya *et al.*, 2015; Rumayor *et al.*, 2015; Kostova, 2017; Zhao *et al.*, 2019; Vassilev and Vassileva, 2023 and references therein). The reduction of anthropogenic Hg emissions can be achieved by the replacement of Hg-rich coals by other solid fuels poor in Hg. For instance, the partial or complete substitution of coal by renewable, C-neutral, and poor in Hg biomass is one of the most promising approaches to diminish Hg emissions from TPPs. Drawing from the long term experience and knowledge on Hg contents in coal and its behaviour during coal combustion, coal replacement aimed at reducing Hg emissions could be done with biomass if this fuel has lower contents and emission rates of Hg than coal during burning, and higher Hg capture in biomass ash than in coal ash.

Although there is some research on Hg contents in biomass and biomass ash (BA), as well as on Hg behaviour and emissions during biomass combustion, the studies about the content, association and modes of occurrence of this element in various biomasses and especially their ashes are scarce (Dare *et al.*, 2001; Demirbaş, 2003; Ericksen *et al.*, 2003; Friedli *et al.*, 2003; Sørnum *et al.*, 2003; Cohen and Dunn, 2004; Fytili and Zabaniotou, 2008; Friedli *et al.*, 2009; Pöykiö *et al.*, 2009; Thy and Jenkins, 2010; Huang *et al.*, 2011; Sarabèr, 2012; Barbosa *et al.*, 2013; Nanda *et al.*, 2013; Nzihou and Stanmore, 2013; Wiinikka *et al.*, 2013; Yossifova and Dimitrova, 2013; Saqib and Bäckström, 2014; Chiarantini *et al.*, 2017; Charvát *et al.*, 2020; Dziok *et al.*, 2020; Méndez-López *et al.*, 2023; Xu *et al.*, 2023; Lei *et al.*, 2024). The Hg concentration in the world reference plant (0.1 ppm) is equal to the coal Clarke value, yet is usually higher than that in the lithosphere, soils, rocks, crude oil, and waters (Table 1). The data reveal that the Hg Clarke values in diverse biomasses (0.015–0.1 ppm) are highly variable (Table 1). For example, particular biomass varieties such as neem, aspen and mango leaves; demolition and eucalyptus wood; wood bark and sawdust; sewage sludge and municipal solid waste; mushrooms, lichens, and wheat straw; can show very high Hg concentrations, namely 0.2–16.4 ppm (Dare *et al.*, 2001; Demirbaş, 2003; Ericksen *et al.*, 2003; Sørnum *et al.*, 2003; Fytili and Zabaniotou, 2008; Nzihou and Stanmore, 2013; Raj and Maiti, 2019; Dziok *et al.*, 2020). In contrast, other biomasses such as an-

Table 1  
Clarke values of Hg (in decreasing order of contents) for plants, coals, rocks, ashes, soils, waters, and other objects, ppm

Object	Hg content	Reference
World reference plant ash <sup>a</sup>	2.0	(Cohen and Dunn, 2004)
Plant ashes	0.10–1.0	(Yudovich and Ketris, 2005c)
Hard coal ashes	0.87	(Ketris and Yudovich, 2009)
Coal ashes	0.75	(Ketris and Yudovich, 2009)
Shales	0.66	(Beus and Grigorian, 1975)
Brown coal ashes	0.62	(Ketris and Yudovich, 2009)
Clays and shales	0.40	(Vinogradov, 1962)
Peats	0.05–0.25	(Madsen, 1981; Nordin, 1994)
Mammal bones	0.10	(Bowen, 1966)
World reference plant	0.10	(Cohen and Dunn, 2004)
Brown coals	0.10	(Ketris and Yudovich, 2009)
Coals	0.10	(Ketris and Yudovich, 2009)
Hard coals	0.10	(Ketris and Yudovich, 2009)
Magmatic rocks	0.08	(Bowen, 1966)
Sedimentary rocks	0.068	(Ketris and Yudovich, 2009)
Mosses	0.06	(Reimann et al., 2001)
Mammals	0.05	(Bowen, 1966)
Lithosphere	0.046	(Beus and Grigorian, 1975)
Plant leaves	<0.04	(Reimann et al., 2001)
Brown algae	0.03	(Bowen, 1966)
Multicellular algae	0.03	(Bowen, 1966)
Soils	0.03	(Bowen, 1966)
Angiospermous plants	0.015	(Bowen, 1966)
Crude oil	0.0035	(Pirrone et al., 2010)
Sea water (mg l <sup>-1</sup> )	0.00003	(Bowen, 1966)
Fresh water (mg l <sup>-1</sup> )	0.00008	(Bowen, 1966)

<sup>a</sup>Theoretic content (without volatilization) calculated from the world reference plant for 4.9% ash yield.

giospermous plants, algae, plant leaves, mosses and mammals have Hg contents lower than that of the world reference plant (Table 1). The Hg contents in plant ashes are commonly in the range of 0.10–1.0 ppm (Yudovich and Ketris, 2005c), whereas Hg concentrations up to 3.7–5.1 ppm were also found in fly ashes from some waste biomasses (Saqib and Bäckström, 2014). The theoretic Hg Clarke value in the world reference plant ash (2.0 ppm) is the highest among the compiled natural or anthropogenic objects, because it is recalculated from Hg content in reference plant without any volatilization during combustion (Table 1).

Data for global biomass burning show annual contribution of Hg emissions to the atmosphere of approximately 675±240 t, which is about 9%, 13% and 29% from the total, natural and anthropogenic Hg sources, respectively (Friedli et al., 2009). This study also reveals that the released Hg from biomass combustion is deposited by dry and wet mechanisms locally and globally and contributes to the formation of toxic bioaccumulating methylmercury species in living tissues. The Hg contents in woody

biomass decrease in the following order: leaves > bark > branches > root > wood (Dziok et al., 2020). Atmospheric Hg is efficiently adsorbed by plants (especially leaves), subsequently transported to the soil by litter fall, and finally assimilated from the soil by roots (Ericksen et al., 2003; Dziok et al., 2020; Méndez-López et al., 2023). The above Hg assimilation process shows that the forests are one of the principal global sinks of anthropogenic and natural Hg within the terrestrial ecosystems (Ericksen et al., 2003; Méndez-López et al., 2023).

Mercury is a biophile metal that occurs in both organic and inorganic form in biomass, as a similar way to coal. However, the Hg hosts in biomass tend to be different than in coal, because the biomass is typically more abundant in organic matter, K, P, Ca, Mg, Cl, Mn, Na, phosphates, and chlorides than coal (Vassilev et al., 2012, 2017). The potential modes of Hg occurrence in biomass are mainly: moisture, organo-metallic compounds, amino acids, functional groups and complexes, methylmercury, and elemental Hg, as well as chlorides, sulphides and oxides of Hg (Bowen, 1966; Cohen and Dunn, 2004;

Thy and Jenkins, 2010; Chiarantini *et al.*, 2017; Raj and Maiti, 2019; Charvát *et al.*, 2020; Gworek *et al.*, 2020; Grace Pavithra *et al.*, 2023). In a similar way to coal, Hg is highly volatile (83–100%) during solid biofuel combustion (Cohen and Dunn, 2004; Thy and Jenkins, 2010; Dziok *et al.*, 2020). The volatilized elemental Hg<sup>0</sup> during coal burning tends to react with flue gas halogens, acid gases, and oxygen to oxidise into Hg<sup>2+</sup> through homogeneous reactions or adsorbed on fly ash particles through heterogeneous reactions (Zhao *et al.*, 2019). It is assumed that various Hg components in biomass are also thermally decomposed to elemental Hg which can react mostly with Cl to form Hg chlorides during biomass combustion (Saqib and Bäckström, 2014). Despite the high Hg volatilization during biomass combustion, BA is abundant in alkaline-earth and alkaline oxyhydroxides, and char, which demonstrate their favourable sorbent properties for the sequestration of CO<sub>2</sub> and other contaminants (including Hg) during biomass combustion and BA storage (Vassilev *et al.*, 2021, 2022). However, detailed knowledge about the modes of Hg occurrence in BA is very scarce.

Aiming to address some of the uncertainties about the occurrence, behaviour, and fate of Hg during biomass combustion outlined above, a study was undertaken to characterize and systematize: (1) Hg content; (2) phase-mineral and chemical composition; (3) association of Hg with other compounds; and (4) potential modes of Hg occurrence in different biomass types and their ashes; as well as (5) volatilization and capture behaviour of Hg during biomass combustion; based on reference data and our own results. The possible environmental advantages or disadvantages related to the ongoing substitution of coal by sustainable biomass in TPPs were also evaluated. The present work is a continuation of our previous studies related to the content, association, potential modes of occurrence, and ecological significance of Hg in Bulgarian coals and coal ashes (Vassilev and Vassileva, 2023) and in diverse biomass types (Vassilev *et al.*, 2024a), as well as the behaviour of Hg during biomass combustion (Vassilev *et al.*, 2024b).

## MATERIALS, METHODS AND DATA USED

The current study integrates a combination of our new results with published data to constrain the content, association, modes of occurrence, thermal behaviour, and environmental significance of Hg related to biomass and biomass ash. Eight biomass

samples and their ashes previously characterized for bulk chemical and phase-mineral composition (Vassilev *et al.*, 2014a, b) were measured for Hg contents and additional mineralogical investigations were also conducted. The selected biomass varieties include: rice husks (RH), switchgrass (SG), beech wood chips (BC), walnut shells (WS), marine macroalgae (MM), sunflower shells (SS), corn cobs (CC), and weathered plum pits (PP). Their ashes (respectively prefixed as RHA, SGA, BCA, WSA, MMA, SSA, CCA and PPA) were produced in an electric oven under static air at 500±10 °C for 2 h and 700±10 °C for 1 h with a heating and cooling rate of 5 °C min<sup>-1</sup>. Notably, the decomposition temperatures of typical Hg compounds such as Hg<sup>0</sup>, Hg<sub>2</sub>Cl<sub>2</sub>, HgCl<sub>2</sub>, humic acid-bound Hg, HgS, Hg(NO<sub>3</sub>)<sub>2</sub>, HgO, Hg<sub>2</sub>SO<sub>4</sub>, HgSO<sub>4</sub>, and pyrite-bound Hg are in the temperature range of 30–640 °C (Zhao *et al.*, 2019), which are lower than the biomass ashing temperature at 700 °C. The selection of the above listed biomass and BA samples is based on their highly variable composition, which is a benefit for comparative studies because they belong to different inorganic types and sub-types of biomasses and BAs (Table 2 and Fig. 1).

The Hg contents in the studied samples were determined by a dual-cell double beam DMA-80 Evo direct mercury analyzer (Milestone Inc.). To characterize sample heterogeneity and offer a representative value for the Hg content, three powdered aliquots (~0.04 g each) from each sample were analysed. The accuracy and reproducibility of Hg analyses by this analytical technique was evaluated through multiple measurements of certified reference material NIST 2702, a marine sediment rich in organic matter (Georgiev and Bidzhova, 2023). The measured Hg contents of the above standard averaged 459.6±27.8 ppb (n = 50 and a standard deviation) which overlaps the certified mean value of 447.4±6.9 ppb. Table 2 shows the calculated average Hg concentrations and standard deviations of the eight biomasses and their ashes. The Hg contents in some additional Bulgarian biomass samples including sunflower stalks, corn stalks, wheat straw, sunflower cake, and rapeseed cake, as well as industrial fly ash produced from sunflower shells at the Astra Bioplant power plant (Bulgaria) were also determined for a comparison.

The composition and properties of biomass and BA samples were studied using light microscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-ray analyser (EDX), inductively coupled plasma – mass spectrometry (ICP-MS), laser abla-

tion (LA) ICP-MS, and through additional ashing, leaching and precipitation procedures (Vassilev *et al.*, 2014a, b). Dry, water-soluble residues (DWRs) were isolated from the BA samples by water leaching and subsequent evaporation and precipitation of the solutions. The leachates from this extraction

procedure were generated from 10 g of samples placed in glass containers with 500 ml of distilled water and soaked for 24 h at ambient temperature. The suspensions were periodically stirred and consequently decanted and filtered. Then, the pH values of the generated water solutions were measured

Table 2

Composition and properties of eight biomass and biomass ash samples (air dried basis) based on (Vassilev *et al.*, 2014b; Vassilev *et al.*, 2024a; Vassilev *et al.*, 2024b), wt.% (indicated otherwise)

Characteristic	Rice husks	Switchgrass	Beech wood chips	Walnut shells	Marine macroalgae	Sunflower shells	Corn cobs	Plum pits
Source	Kovachevo, Bulgaria	Mead, USA	Rosenberg, Germany	Debnevo, Bulgaria	Tsarevo, Bulgaria	Billa, Bulgaria	Debnevo, Bulgaria	Debnevo, Bulgaria
<i>1. Biomass</i>								
Sample code	RH	SG	BC	WS	MM	SS	CC	PP
Mean Hg content (ppb) for n = 3 <sup>a</sup>	11.13	6.20	3.30	14.96	17.67	2.53	43.30	2.85
Standard deviation (ppb)	13.96	1.76	0.47	1.40	1.36	0.23	13.34	0.31
Ash yield (500 °C/2h)	18.5	5.1	1.3	0.9	28.2	3.0	2.1	0.7
Ash yield (700 °C/1h)	17.5	4.2	0.9	0.8	23.6	2.4	1.7	0.5
<i>2. Biomass ash (500 °C/2h)</i>								
Sample code	RHA	SGA	BCA	WSA	MMA	SSA	CCA	PPA
Inorganic type	S	S	C	CK	K	K	K	CK
Inorganic sub-type	S-HA	S-MA	C-LA	CK-LA	K-LA	K-LA	K-LA	CK-LA
Mean Hg content (ppb) for n = 3	3.16	12.58	17.30	20.28	24.83	25.52	31.22	45.23
Standard deviation (ppb)	0.01	0.09	1.99	0.14	3.80	1.02	0.31	1.00
Theoretic mean Hg content <sup>b</sup> (ppb) for n = 3	60.16	121.57	253.85	1662.22	62.66	84.33	2061.90	407.14
Hg volatilization at 500 °C (%)	95	90	93	99	60	70	98	89
pH of leachate	8.1	9.8	12.1	10.5	8.4	12.9	11.3	8.9
DWR	3.9	23.3	20.2	41.1	42.8	29.8	45.1	9.4
SiO <sub>2</sub>	89.86	62.90	5.48	2.84	5.60	1.45	36.67	12.01
CaO	1.40	7.69	62.58	38.11	22.06	15.57	2.12	43.95
K <sub>2</sub> O	4.16	18.77	18.00	49.33	7.56	49.84	47.57	16.29
MgO	0.49	4.20	7.49	3.80	7.69	11.87	1.97	4.18
P <sub>2</sub> O <sub>5</sub>	0.60	2.44	2.49	2.37	0.97	6.54	4.82	10.17
Al <sub>2</sub> O <sub>3</sub>	1.04	0.89	0.49	0.52	0.98	0.12	0.81	2.57
SO <sub>3</sub>	1.31	2.17	0.77	2.03	28.49	11.39	3.44	7.72
Fe <sub>2</sub> O <sub>3</sub>	0.41	0.42	0.36	0.40	0.69	1.32	1.50	1.75
Na <sub>2</sub> O	0.23	0.11	0.11	0.12	14.07	0.22	0.28	0.79
Cl <sub>2</sub> O	0.21	0.23	0.09	0.38	11.84	1.60	0.69	0.27
MnO	0.27	0.14	2.11	0.05	0.02	0.07	0.07	0.14
TiO <sub>2</sub>	0.02	0.04	0.03	0.05	0.03	0.01	0.06	0.16
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> +TiO <sub>2</sub>	91.33	64.25	6.36	3.81	7.30	2.90	39.04	16.49
CaO+MgO+MnO	2.16	12.03	72.18	41.96	29.77	27.51	4.16	48.27
K <sub>2</sub> O+P <sub>2</sub> O <sub>5</sub> +SO <sub>3</sub> +Cl <sub>2</sub> O+Na <sub>2</sub> O	6.51	23.72	21.46	54.23	62.93	69.59	56.80	35.24
<i>3. Biomass ash (700 °C/1h)</i>								
Mean Hg content (ppb) for n = 3–6	4.60	3.61	31.20	21.67	27.60	13.50	8.24	44.26
Standard deviation (ppb)	0.05	0.03	1.03	0.52	1.10	0.11	0.05	1.98
Theoretic mean Hg content <sup>c</sup> (ppb) for n = 3–6	63.60	147.62	366.67	1870.00	74.87	105.42	2547.06	570.00
Hg volatilization at 700 °C (%)	93	98	92	99	63	87	100	92

<sup>a</sup> Six measurements for sample CC.

<sup>b</sup> Calculated from the Hg concentration in biomass and the ash yield data at 500 °C/2h.

<sup>c</sup> Calculated from the Hg concentration in biomass and the respective ash yield data at 700 °C/1h.

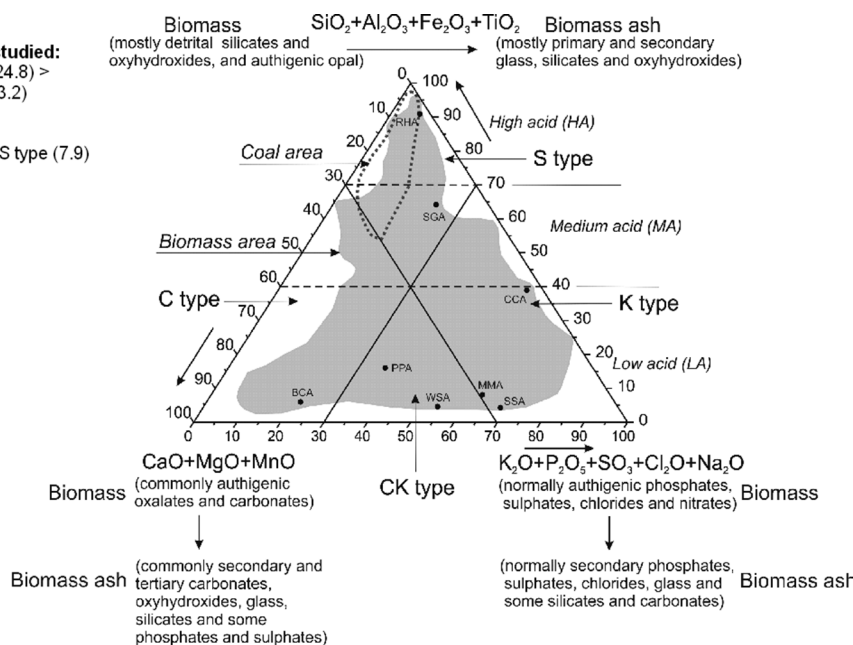
Abbreviations: db, air-dried basis; DWR, dry water-soluble residue; n, number of measurements.

**Hg values (ppb) in 8 biomass ashes (500°C) studied:**  
 PPA (45.2) > CCA (31.2) > SSA (25.5) > MMA (24.8) >  
 WSA (20.3) > BCA (17.3) > SGA (12.6) > RHA (3.2)

**Mean Hg values (ppb) in biomass ash types:**  
 CK type (32.8) > K type (27.2) > C type (17.3) > S type (7.9)

**Abbreviations:**

BCA, beech wood chips ash  
 CCA, corn cobs ash  
 MMA, marine macroalgae ash  
 PPA, plum pits ash  
 RHA, rice husks ash  
 SGA, switchgrass ash  
 SSA, sunflower shells ash  
 WSA, walnut shells ash



**Fig. 1.** Mercury contents in eight biomass ash samples and their position with areas of 141 biomass ash varieties and 38 coal ashes in the chemical classification system of inorganic matter in biomass and biomass ash (based on Vassilev and Vassileva, 2019), wt.%.

by a bench pH meter. Finally, the leachates were placed in a drying oven at 80 °C for evaporation and crystallization, yielding the DWRs. The contents of 12 ash-forming elements in BAs were determined by: ICP-MS for Mn; LA-ICP-MS for Ca, Mg, K, Na, Si, P, Al, Fe, and Ti; SEM-EDX for S and Cl as explained earlier (Vassilev *et al.*, 2014b). The Hg concentrations in some minerals identified in biomass and BA samples enriched in this element were also determined by SEM-EDX.

## RESULTS AND DISCUSSION

### Composition and some properties of biomass ash

Characterization of the bulk chemical and phase-mineral composition and properties of the biomass combustion residues are among the most important parameters for understanding Hg behaviour during biomass combustion. General information about this composition and certain important properties of BA have been provided in earlier publications (Vassilev *et al.*, 2010, 2017).

The chemical composition of the studied BAs (Table 2) is highly variable and particularly for: SiO<sub>2</sub> (1–90%), CaO (1–63%), K<sub>2</sub>O (4–50%), Na<sub>2</sub>O (0.2–14%), Cl<sub>2</sub>O (0.1–12%), MgO (0.5–12%), SO<sub>3</sub>

(1–11%), and P<sub>2</sub>O<sub>5</sub> (0.6–10%). The description of bulk chemical composition of BA is an irreplaceable stage; however, it is insufficient for an explanation of the behaviour of an element during biomass combustion. For that purpose, a knowledge about the association and modes of occurrence of Hg in specific phases and minerals of BA is necessary.

Biomass ash is a complex heterogeneous mixture of inorganic matter and, to a lesser extent, organic matter containing numerous solid and fluid intimately associated phases or minerals formed mostly during biomass combustion. The inorganic matter of BAs produced at 500 °C (Table 3) comprises both amorphous and crystalline matter represented by silicates (quartz, kalsilite, and leucite), oxides and hydroxides (portlandite and periclase), phosphates (apatite and whitlockite), sulphates (anhydrite and arcanite), carbonates (calcite, kalicinite, butschliite, and fairchildite), and chlorides (sylvite and halite). The organic matter consists of char which occurs only at trace contents in BA. On the other hand, the phases and minerals identified in the eight studied biomass samples include organic matter (cellulose, hemicellulose, and lignin), chlorides (halite and sylvite), nitrates (Ca nitrate hydrate and nitrocalcite), oxalates (weddelite and whewellite), carbonates (calcite and magnesite), sulphates (arcanite), and silicates (opal) (Vassilev *et al.*, 2012). Hence, the phases and minerals in BA can be pri-

Table 3

Contents of inorganic phases and minerals identified by XRD in eight biomass ashes produced at 500 °C based on (Vassilev *et al.*, 2014a), wt.%

Phase, mineral	Formula	RHA	SGA	BCA	WSA	MMA	SSA	CCA	PPA
1. Inorganic amorphous matter		83	65	32	39	42	44	45	32
2. Inorganic crystalline matter		17	35	68	61	58	56	55	68
2.1. Silicates		3	13	2		1		10	7
Kalsilite (Ks)	KAlSiO <sub>4</sub>							5	
Leucite (Le)	KAlSi <sub>2</sub> O <sub>6</sub>		7					3	
Quartz (Q)	SiO <sub>2</sub>	3	6	2		1		2	7
2.2. Oxides and hydroxides						7	3		
Periclase (Peri)	MgO						3		
Portlandite (Port)	Ca(OH) <sub>2</sub>					7			
2.3. Phosphates				10					5
Apatite (Ap)	Ca(PO <sub>4</sub> ) <sub>3</sub> (Cl,F,OH,CO <sub>3</sub> )								5
Whitlockite (Wl)	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>			10					
2.4. Sulphates		9	2		2	11	30	2	2
Anhydrite (A)	CaSO <sub>4</sub>		2		2	11	2	2	2
Arcanite (Arc)	K <sub>2</sub> SO <sub>4</sub>	9					28		
2.5. Carbonates			20	56	59	19	23	40	54
Butschliite (Bu)	K <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub>				11				
Fairchildite (F)	K <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub>				26		10		2
Calcite (Cc)	CaCO <sub>3</sub>		20	56	18	19	8		52
Kalicinite (K)	KHCO <sub>3</sub>				4		5	40	
2.6. Chlorides		5				20		3	
Halite (Ha)	NaCl					18			
Sylvite (Sy)	KCl	5				2		3	

primary (original) pre-combustion minerals in biomass, new secondary minerals and phases formed during biomass combustion, and new tertiary post-combustion minerals formed during BA storage and weathering. The eight BAs belong to the “S” (RHA and SGA), “C” (BCA), “K” (CCA, MMA, and SSA) and “CK” (PPA and WSA) inorganic types based on their specific phase-mineral and chemical composition (Table 2 and Fig. 1).

The water-soluble fraction of BA contains various mobile components with either favourable or harmful ecological and technological significance. The yield of this fraction from the eight BAs (Table 2) is 4–45% (mean 27%). Hence, the mineralization of these solutions has sea saline and brine character according to the classification for natural waters (Perelman, 1989). The reason for the high DWR contents in BAs is the intensive formation of water-soluble inorganic matter generated from both organic and inorganic matter during biomass combustion at 500 °C. The decreasing order of DWR yields from BAs is as follows: CCA > MMA >

WSA > SSA > SGA > BCA > PPA > RHA; while the mean DWR values for different inorganic types of BAs are: “K” type (39%) > “CK” type (25%) > “C” type (20%) > “S” type (14%). The diverse phase-mineral transformations among the inorganic biomass types during biomass combustion are the reason for such differences as discussed elsewhere (Vassilev *et al.* 2013 and Vassilev *et al.*, 2014a). For example, BAs among the “K”, “CK” and “C” types are normally enriched in soluble salts such as carbonates, oxyhydroxides, phosphates, sulphates, and chlorides, whereas the “S” type BAs are commonly abundant in less soluble silicates and inorganic amorphous matter (Table 3).

The pH values of the eight BA leachates are 8.1–12.9 (mean 10.3), confirming their moderately to highly alkaline character (Table 2). The decreasing order of pH values for these BA solutions is: SSA > BCA > CCA > WSA > SGA > PPA > MMA > RHA. The mean pH values for the various inorganic types of BAs systematically increase from “S” type (pH 9) to “CK” type (pH 10) to “K”

type (pH 11), and to “C” type (pH 12). The increasing pH from the “S” to “C” BA types reflect the intensive formation of water-soluble Ca, Mg, K and Na oxyhydroxides, carbonates, and bicarbonates in these BA types (Vassilev and Vassileva, 2019). It is well known that the water solubility for most elements in BAs is pH sensitive (Izquierdo and Querol, 2012). For example, the more alkaline character of BAs causes greater release of oxyanionic-forming species of elements such as As, B, Cr, F, Mo, Sb, Se, V, and W, and lower mobility of a large number of species containing siderophile and chalcophile elements, precisely Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Sn, Ti, Zn, and others (Izquierdo and Querol, 2012; Vassilev and Vassileva, 2019).

The summarized data show that the composition and properties of the studied BAs are highly variable and depend mostly on the type of combusted biomass. The sample selection covers a wide range of BA types and sub-types and provides a good overview on the composition and properties, as well as variable Hg contents of BAs in general (see below).

### Mercury in biomass ash

The Hg contents in BA commonly vary between 0.1 ppm and 1.0 ppm, which is relatively high in comparison with other objects (Table 1). However, the reference data also reveal very high Hg concentrations in particular BAs such as: 7.3 ppm in sewage sludge ash (Cenni *et al.*, 2001); 3.0 ppm in pine sawdust fly ash (Ross *et al.*, 2002); 2.8 ppm in wood ash (Someshwar, 1996); 1.2 ppm in spruce wood ash (Reimann *et al.*, 2008) and wood fly ash (Thy and Jenkins, 2010). In contrast, there are BA varieties with very low Hg contents such as: 0.002 ppm in miscanthus ash (Richaud *et al.*, 2004); 0.006 ppm in ashes from conifer wood, Jose tall wheat grass, rice straw, and wheat straw; 0.007 ppm in ashes from athel wood, creeping wild rye, and eucalyptus wood (Thy and Jenkins, 2010); and 0.008 ppm in pine sawdust ash (Ross *et al.*, 2002).

The eight studied biomass samples (Table 2) have Hg contents between 0.003 and 0.043 ppm (mean 0.013 ppm), which is about an order of magnitude lower than the Clarke values for biomass (0.1 ppm) and coal (0.1 ppm). Their ashes produced at 500 °C (Table 2) show Hg concentrations of 0.0032–0.0452 ppm (mean 0.0225 ppm), which are much lower than the typical Hg contents in BA (0.1–1.0 ppm) and coal ash (0.75 ppm) listed in Table 1. The measured Hg concentrations in BAs decrease in the following order: PPA > CCA > SSA >

MMA > WSA > BCA > SGA > RHA, whereas the mean contents for ash types are: “CK” type > “K” type > “C” type > “S” type (Fig. 1).

Notably, the mean Hg contents of “CK” (0.0328 ppm for PPA and WSA) and “K” (0.0272 ppm for CCA, MMA, and SSA) inorganic types are significantly higher compared with the mean concentrations in other inorganic types such as “C” type (0.0173 ppm for BCA) > “S” type (0.0079 ppm for SGA and RHA) listed in Fig. 1. It seems that certain newly formed minerals identified in these BAs (Table 3) such as phosphates (apatite and whitlockite), sulphates (anhydrite and arcanite), chlorides (halite and sylvite), carbonates (butschliite, fairchildite, calcite, and kalicinite), and oxyhydroxides (periclase and portlandite) that are typical for the “CK” and “K” ash types (Fig. 1), play some role as host matrices for the Hg distribution and retention.

The sample PPA has the highest Hg content (0.0452 ppm) among the studied BAs (Table 2). Therefore, a more detailed description of this BA variety is essential for the evaluation of Hg distribution. It belongs to the “CK” inorganic type and low acid (“CK-LA”) sub-type (Fig. 1) and exhibits some distinctive chemical and mineral characteristics in comparison with other BAs such as: (1) relative enrichment in Al, Ca, Fe, Na, P, S, Ti, inorganic crystalline matter, quartz, apatite, and calcite; and (2) relative depletion in ash yield, DWR, inorganic amorphous matter, oxyhydroxides, sulphates, and chlorides (Tables 2 and 3). The combination of these two characteristic features seems to favour the relative enrichment of Hg in PPA compared to other BA varieties. In contrast, the lowest Hg content among the studied BA samples is recorded in RHA (0.0032 ppm). This ash belongs to “S” inorganic type and high acid (“S-HA”) sub-type (Fig. 1), and also shows some distinctive chemical and mineral features in comparison with other BAs, namely: (1) relative enrichment in ash yield, Mn, Si, inorganic amorphous matter, sulphates, and chlorides; and (2) relatively low values of pH, DWR, Ca, Fe, K, Mg, P, S, Ti, inorganic crystalline matter, oxyhydroxides, phosphates, and carbonates (Tables 2 and 3). The combination of these two characteristic features seems to suppress the relative enrichment of Hg in RHA compared to other BA varieties. In fact, most enrichment or depletion trends for the characteristics of RHA are opposite to those of PPA, suggesting that some of their contrasting properties indeed control the Hg retention in BAs.

In summary, the Hg contents of the studied BAs are variable, but generally lower than the typical Hg concentrations in BA and coal ash worldwide. The



Hg contents in BA depend primary on BA types, as well as composition and origin of BA.

### Association of mercury in biomass ash

The correlation analysis between Hg concentration and other characteristics in BA gives a preliminary information for understanding some basic trends and associations of this element in the BA system (Vassilev *et al.*, 2014b). The statistically significant positive correlations of Hg with major elements confirms the association of Hg with minerals or phases containing such major elements in BA. These correlations are the result both of indirect (coexistence of mineral assemblages) or direct (mineral parageneses and generations) genetic associations of Hg in BA. The statistically significant positive correlation between an element and phase does not specify that this phase is the main host of that element, whereas some statistically insignificant correlations could be important in the BA system. Therefore, further indirect and especially direct studies, as well as literature data connected with the modes of Hg occurrence in BA should always be considered in conjunction with the correlation tests (see below).

Our previously reported results for Hg contents in the studied biomass samples (Vassilev *et al.*, 2024a) show that there are: (1) a significant positive correlation between Hg and ash yield, N, Cl, and S, as well as relatively strong but statistically insignificant positive correlation values between Hg and fixed carbon, hemicellulose, DWR, pH, electrical conductivity, Na, and the sum of K+P+S+Cl+Na; and (2) a significant negative correlation between Hg and volatile matter and P, as well as relatively strong but statistically insignificant negative correlation values between Hg and C, cellulose, Fe, Mn,

Mg, Ti, Ca, and the sum of Ca+Mg+Mn. However, results from this study (Table 4) show that compared with biomass samples, Hg for BA samples reveal different Hg correlations. For example, in BAs there are: (1) a significant positive correlation between Hg and Fe, P, Ti, and inorganic crystalline matter, as well as relatively strong but statistically insignificant positive correlation between Hg and Al and carbonates; and (2) a significant negative correlation between Hg and inorganic amorphous matter, as well as relatively strong but statistically insignificant negative correlation between Hg and ash yield and Si (Fig. 2). Therefore, the association of Hg with unstable phases in biomass shifts to a Hg association with relatively more stable phases in BA during biomass combustion (see the discussion below).

The summarized data reveal that Hg in the studied BA samples correlates preferentially with specific stable components such as Fe-, P-, Ti- and Al-bearing minerals and phases, despite the diverse and complex BA composition and origin. It can be supposed that different fixation mechanisms and modes of occurrence of Hg are involved in this BA system.

### Mercury volatilization and capture behaviour during biomass combustion

The knowledge achieved about Hg during coal combustion can be used as a supplementary interpretation of Hg behaviour during biomass burning. For instance, the volatilization temperatures of Hg and some Hg components during coal combustion have been determined for: total Hg (25–69% up to 300 °C); HCl-soluble mercury (150–600 °C); organically bound Hg (220–600 °C); pyrite bound Hg (250–630 °C); inorganic forms of Hg (600 °C); and

Table 4

Correlation coefficient values ( $R^2$ )<sup>a</sup> between Hg contents in eight biomass ashes produced at 500°C and other characteristics for these biomass ashes

Element	Correlation coefficient value of Hg with:
Hg	(+) <b>Fe<sub>2</sub>O<sub>3</sub>(0.86)</b> ; <b>P<sub>2</sub>O<sub>5</sub>(0.85)</b> ; <b>TiO<sub>2</sub>(0.77)</b> ; <b>ICM(0.75)</b> ; Car(0.56); Al <sub>2</sub> O <sub>3</sub> (0.55); K <sub>2</sub> O+P <sub>2</sub> O <sub>5</sub> +SO <sub>3</sub> +Cl <sub>2</sub> O+Na <sub>2</sub> O(0.53); CaO(0.31); CaO+MgO+MnO(0.31); SO <sub>3</sub> (0.30); K <sub>2</sub> O(0.28); DWR(0.21); MgO(0.21); Pho(0.19); pH(0.12); Sil(0.12); Na <sub>2</sub> O(0.11); Oxi(0.11); Cl <sub>2</sub> O(0.10)
	(-) <b>IAM(-0.75)</b> ; SiO <sub>2</sub> (-0.61); SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> +TiO <sub>2</sub> (-0.58); A(-0.34); MnO(-0.22); Hgv (-0.17); Chl(-0.04); Sul(-0.02)

<sup>a</sup> The significant  $R^2$  values at 95% confidence level are:  $\geq 0.63$  and  $\leq -0.63$  for 8 variables (in bold font).

Abbreviations: A, ash yield; Car, carbonates; Chl, chlorides; DWR, dry water-soluble residue; Hgv, Hg volatilization; IAM, inorganic amorphous matter; ICM, inorganic crystalline matter; Oxi, oxides and hydroxides; pH, acidity or alkalinity; Pho, phosphates; Sil, silicates; Sul, sulphates.

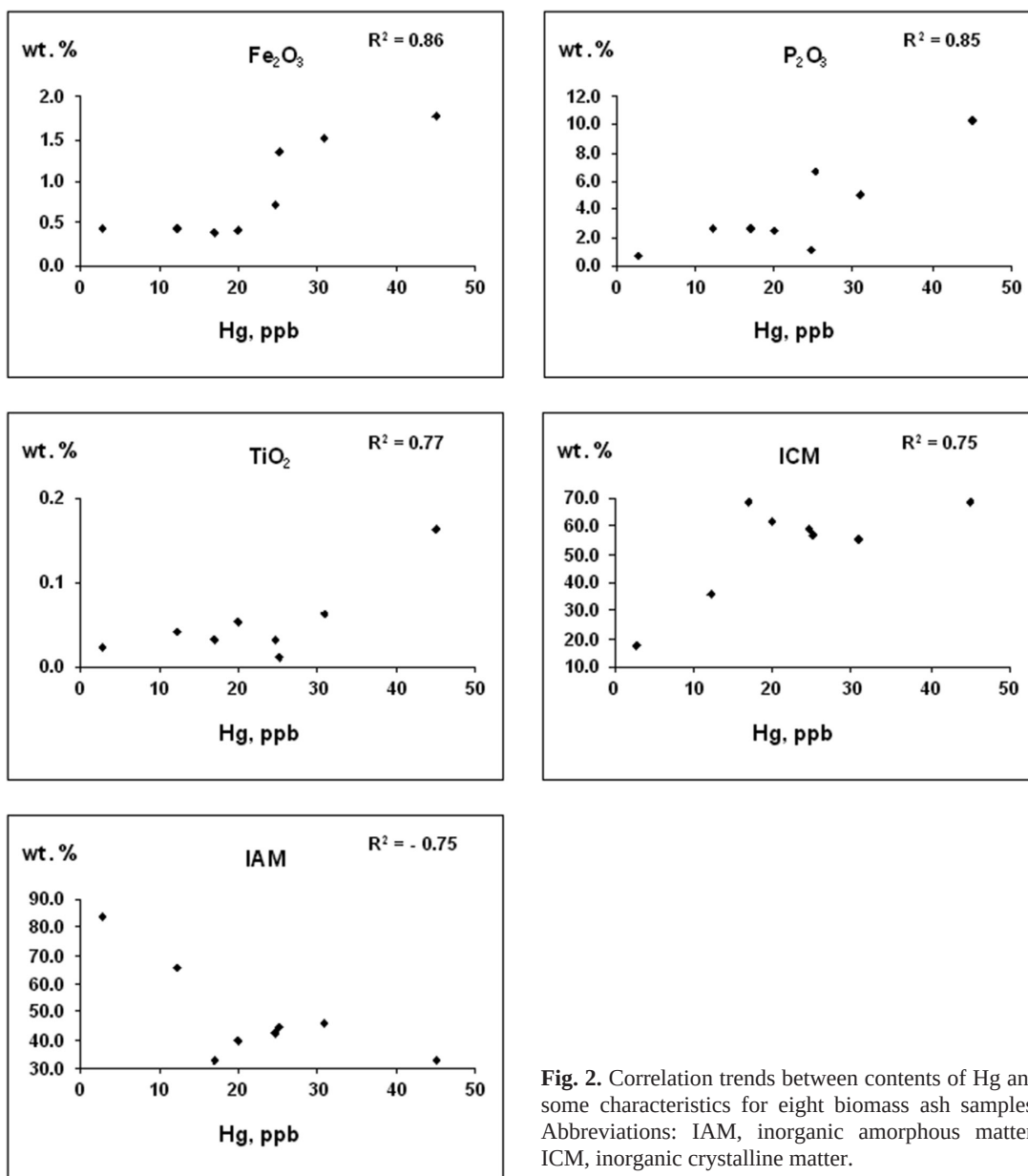


Fig. 2. Correlation trends between contents of Hg and some characteristics for eight biomass ash samples. Abbreviations: IAM, inorganic amorphous matter; ICM, inorganic crystalline matter.

silicate bound Hg (>600 °C) (Strezov *et al.*, 2010; Zhao *et al.*, 2019; Dziok *et al.*, 2020). When the flue gas cools during coal combustion, the released elemental Hg<sup>0</sup> can react with flue gas halogens (Cl<sub>2</sub>, Br<sub>2</sub>), acid gases (HCl, HBr, NO<sub>2</sub>), and O<sub>2</sub> to oxidise mainly into Hg<sup>2+</sup> through homogeneous reactions, whereas a portion of the volatilized Hg<sup>0</sup> can also be absorbed on fly ash particles through heterogeneous reactions (Zhao *et al.*, 2019). For example, the elemental Hg in flue gases may be oxidized to HgCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, HgSO<sub>4</sub>, HgBr<sub>2</sub>, HgI<sub>2</sub>, HgS, HgO, HgSe, and others (Yudovich and Ketris, 2005b; Saqib and Bäckström, 2014; Charvát *et al.*, 2020). As a result,

limited portions of the volatilized Hg are captured, mostly by char, Ca sulphate, as well as Fe, Al and Ti oxides in coal fly ashes (Lopez-Anton *et al.*, 2009; Hower *et al.*, 2010; Ariya *et al.*, 2015; Kostova *et al.*, 2016; Zhao *et al.*, 2019; Vassilev and Vassileva, 2023).

Similar to coal, the reference data also shows that Hg has high volatilization behaviour during solid biofuel combustion, namely: 83–99% (average 90%) at 300 °C (Dziok *et al.*, 2020), >90% at 500 °C (Cohen and Dunn, 2004), and complete release at 575 °C (Thy and Jenkins, 2010). Most Hg is emitted in the form of gaseous elemental Hg during

low temperature biomass combustion, whereas gaseous oxidized mercury ( $\text{Hg}^{2+}$ ) can be the dominant species during high temperature biomass combustion (Huang *et al.*, 2011). The Hg behaviour during biomass combustion was evaluated herein based on our new results and published data. The present data include the measured Hg contents of various biomasses and their ashes produced at 500 °C and 700 °C (Table 2) to calculate the Hg volatilization during combustion of these eight biomasses. The volatilization behaviour of Hg was calculated based on Hg contents determined in the biomass samples and BAs (on air dried basis) produced at both temperatures, as well as on the theoretical Hg concentrations in BAs (without volatilization) calculated on ash yield basis for biomass samples incinerated at the respective temperatures. Thus, the theoretical Hg contents in BAs were used for Hg balance calculations during biomass combustion at 500 °C and 700 °C (Table 2). These proximate estimations show that the Hg volatilization occurs as follows:

(1) WSA (99%) > CCA (98%) > RHA (95%) > BCA (93%) > SGA (90%) > PPA (89%) > SSA (70%) > MMA (60%) at 500 °C.

(2) CCA (100%) > WSA (99%) > SGA (98%) > RHA (93%) > BCA = PPA (92%) > SSA (87%) > MMA (63%) at 700 °C.

It can be seen that the Hg volatilization is 60–99% (mean 87%) at 500 °C and 63–100% (mean 91%) at 700 °C. Generally, the Hg release slightly increases with increasing temperature, as only BCA and RHA show very low (1–2%) negative fluctuations. The volatilization increase with temperature matches the general observation for increasing volatility of trace elements with furnace temperature due to their increasing vapour pressure (Saqib and Bäckström, 2014). On the other hand, the calculations for BA types reveal that the mean Hg volatilization is as follows:

(1) “CK” (94%) > “S” = “C” (93%) > “K” (76%) at 500 °C.

(2) “CK” = “S” (96%) > “C” (92%) > “K” (83%) at 700 °C.

Hence, the Hg release for BAs and ash types occurs in a similar to almost identical decreasing order at both temperatures. The volatilized Hg proportions generally match the previously published literature data noted above. However, the highest Hg release occurs for the “CK”, “S” and “S” ash types, whereas the lowest Hg volatilization is observed for the “K” ash type. Therefore, the BAs from the “K” type (MMA and SSA) that are enriched in K-, P-, S-, Cl- and Na-bearing components (Fig. 1) show the highest capture potential, namely 30–40% at

500 °C and 13–37% at 700 °C (Table 2). These samples are commonly enriched in DWR, Cl, K, Mg, Na, P, S, portlandite, periclase, anhydrite, arcanite, halite, sylvite, and fairchildite in comparison with other BAs (Tables 2 and 3). Thus, the combination of some water-soluble salts such as oxyhydroxides, sulphates, chlorides, and partly carbonates (Table 3) with well-known sorbent properties is likely responsible for the increasing sequestration of Hg in these BAs. However, most of these minerals have decomposition or melting temperatures between 700 and 1200 °C (Vassilev *et al.*, 2013) and Hg might be completely volatilized once these temperatures are reached. The current study additionally indicates that some stable Fe-, P-, Ti- and Al-bearing minerals and phases, as well as less stable chlorides could also affect the capture of Hg in BA (Table 4).

In summary, the data show that about 60–99% (mean 87%) and 63–100% (mean 91%) of Hg in biomass were volatilized at 500 °C and 700 °C, respectively, and only limited parts of Hg were captured by particular BAs enriched in salts such as carbonates, oxyhydroxides, phosphates, sulphates, and chlorides.

### Potential modes of mercury occurrence in biomass ash

The published data on the modes of Hg occurrence in BA are very limited because the high volatilization of this element during biofuel combustion (>83%), as well as the low Hg content (ppb level) in the combustion products pose serious analytical challenges to the determination of concentration, modes of occurrence, thermal behaviour, and fate of Hg (see below). Therefore, the present study mostly discusses assumptions, indirect observations based on correlations and associations and, to a lesser extent, direct observations about the potential modes of Hg occurrence in BA.

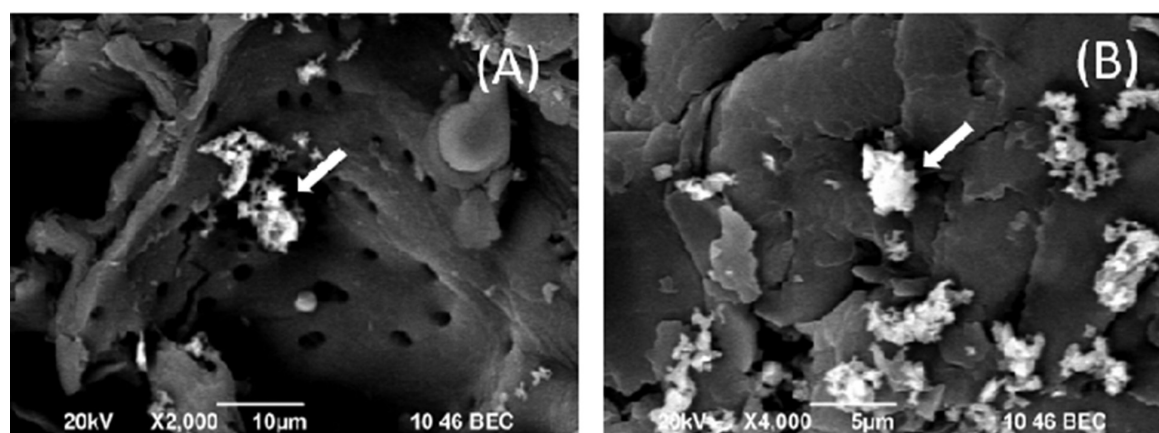
The available detailed knowledge for modes of Hg occurrence in coal and coal ash can be implemented in the field of biomass and BA. The modes of Hg occurrence in coal and coal ash include: (1) organic matter; (2) isomorphous occurrence in sulphides, sulfosalts, and selenides; (3) specific Hg minerals; and (4) impurities in silicates, carbonates, and other minerals (Vassilev *et al.*, 2024a) and references therein). On the other hand, the published studies identify multiple potential modes of Hg in biomass such as: free cation in moisture; organometallic compounds; amino acids; tannic acid; Hg-cysteine, sulfhydryl/thiol groups of proteins (SHgS), functional groups and complexes; methyl-

dimethyl-, ethyl-, and phenyl-mercury; and organic salts; as well as elemental Hg and certain chlorides, sulphides and oxides of Hg (Bowen, 1966; Cohen and Dunn, 2004; Thy and Jenkins, 2010; Chiarantini *et al.*, 2017; Raj and Maiti, 2019; Charvát *et al.*, 2020; Gworek *et al.*, 2020; Grace Pavithra *et al.*, 2023). The specific modes of Hg occurrence in BA are undefined, but it was supposed that the fate of vaporized mercury in the combustor stack is controlled by cooling homogeneous and heterogeneous reactions with chemical deposition on char and ash particles or boiler surfaces as oxides, sulphates and halides (Schofield, 2008; Hower *et al.*, 2010; Thy and Jenkins, 2010).

Our former results for Hg contents in the eight studied biomass samples indicate that Hg occurs in both organic and inorganic matter of the biomass (Vassilev *et al.*, 2024a). The preferential association and potential modes of occurrence of Hg comprise hemicellulose and water-soluble Cl-, S-, N-, and Na-bearing phases and minerals including chlorides, sulphates, and nitrates such as halite, sylvite, arcanite, Ca nitrate, and nitrocalcite (Vassilev *et al.*, 2024a). However, the present study for Hg in the eight BA samples shows completely different correlations for this element (Table 4). Mercury in these BAs preferentially associates with more stable minerals and phases which could be potential modes of Hg occurrence as possible impurities in these host matrices of BA. Hence, the above associations indicate that the unstable and volatile forms of Hg in biomass transform to relatively more stable Hg-containing minerals and phases that capture some of the volatilized Hg in BA. This is a result of intensive Hg volatilization accompanied by some

subsequent reactions of Hg with inorganic crystalline matter such as Fe-, P-, Ti-, Al-bearing phases during biomass combustion (Table 4). In contrast, Hg does not reveal association with inorganic amorphous matter and Si-containing phases in the studied BA system (Table 4). The above observations require a special consideration. The P and Al minerals identified by XRD in the present BAs (Table 3) include Ca phosphates (apatite and whitlockite) and K aluminosilicates (kalsilite and leucite), whereas specific Fe and Ti minerals were not found by this method due to the low contents of these elements in BAs. For example, the concentrations of Fe and Ti oxides in the studied BAs are only 0.36–1.75% and 0.01–0.16%, respectively (Table 2). However, the Fe, Al and Ti oxyhydroxides (mostly hematite,  $\gamma$ - $\text{Al}_2\text{O}_3$ , and rutile) are common minerals in BAs enriched in these elements (Vassilev *et al.*, 2013). For instance, some metal oxides such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  were reported to benefit  $\text{Hg}^0$  oxidation to  $\text{Hg}^{2+}$  or adsorption in coal fly ash (Ariya *et al.*, 2015; Zhao *et al.*, 2019). These studies explain the capture of Hg by Fe oxyhydroxides (mainly hematite, magnetite, maghemite, and goethite) and Al oxide ( $\gamma$ - $\text{Al}_2\text{O}_3$ ) in ash. Hence, our results are in good agreement with the reference data and confirm some similarities in Hg behaviour during coal and biomass combustion. On the other hand, the affinity of Hg to P-containing phases and inorganic crystalline matter in ash was not reported in the literature, whereas inorganic amorphous matter seems to have poor sequestration of Hg in ash.

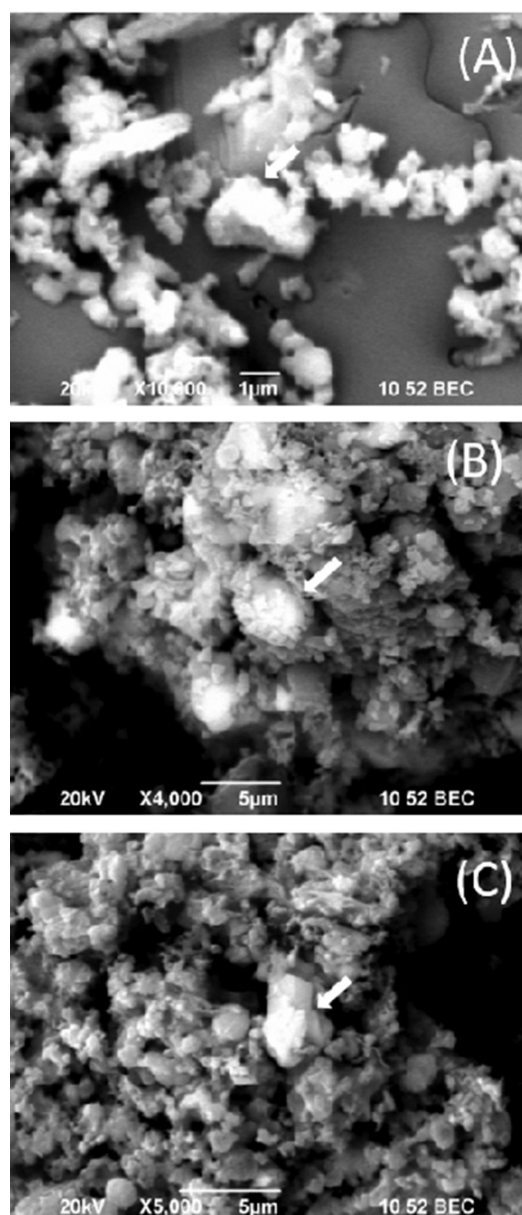
To directly confirm the Hg modes of occurrence in the BA samples, some investigations by SEM-EDX were conducted for numerous particles



**Fig. 3.** SEM images of CC: (A) Kalsilite or leucite grain enriched in Hg (2.1%); and (B) Kalsilite or leucite grain enriched in Hg (0.6%).

among the most Hg-rich samples, namely CC and CCA produced at 500 °C (Table 2). The results show that about 0.6–2.1% Hg were measured in K aluminosilicate mineral (kalsilite or leucite) represented by grains with size of 5–10 µm in the CC sample (Fig. 3). Additionally, significant occurrence of Hg (0.2–0.6%) in kalsilite or leucite grains and sylvite crystals with a size of about 5 µm were also found in the CCA sample (Fig. 4). Kalsilite, leucite and sylvite are common minerals in CCA (Table 3). Finally, trace contents of Hg in Fe oxide minerals (probably hematite) were also identified in the CCA sample. These results represent a direct confirmation of the Hg occurrence as impurities in particular K, Al, Si, Cl and Fe minerals in the CC and CCA samples. The CC sample is the most enriched in Hg (Table 2) and our previous study shows that this sample has quite different position, trend, and behaviour, as well as specific composition and properties in comparison with the other biomass samples (Vassilev *et al.*, 2024a). This corn cob sample was stored long-term for several years in a bunker under natural conditions in contrast to the other fresh biomass samples. Therefore, an additional incorporation of air and particular Hg in the sample may have raised its total Hg contents. The ash yield (informative for dust contamination) has an intermediate value for CC; however, this sample is enriched in typically less mobile Si, Fe, and Ti components (Table 2), which are characteristic of soil contamination in the biomass system (Vassilev *et al.*, 2017). Additionally, the CC sample has much higher Hg content and ash yield value in comparison with the fresh PP and WS samples collected from the same area (Table 2). Finally, it is well known that large particle fractions of biomass have higher cellulose, hemicellulose and lignin concentrations, and lower ash content than small particle fractions (Tamaki and Mazza, 2010). Our results show that the finest fraction (<200 µm) of the CC sample is enriched in Hg (0.82 ppm), which reveals a dominant inorganic Hg affinity. Combined, these observations indicate a possible particulate Hg contamination in the CC sample.

The reference data and our results confirm the complex character of associations and forms of Hg in BA. Despite the above indirect and direct observations, the modes of Hg occurrence in BA are still unclear because this trace element could be present as: discrete minerals and phases; impurities (isomorphously or in defect sites) of the crystal structures; impurities in host matrices of inorganic amorphous and semi-crystalline matter or organic matter (char); ion-exchanged and adsorbed forms in/on mineral and char matrices and surfaces; dis-



**Fig. 4.** SEM images of CCA: (A) Kalsilite or leucite grain enriched in Hg (0.6%); (B) sylvite crystals enriched in Hg (0.2%); (C) sylvite crystals enriched in Hg (0.5%).

solved ions in moisture or gas–liquid inclusions in some minerals or phases. Therefore, the identification of Hg in discrete forms or as impurities in specific phases and minerals is a challenging task. For that purpose, a combination of various approaches and methods are required, namely: (1) direct methods (electron and light microscopy); and (2) indirect methods such as correlation analysis, XRD and spectroscopic investigations of physically or chemically separated fractions, as well as sequential leaching procedures with subsequent determination

of Hg contents in the produced fractions, leachates and their residues. Such future investigations will be conducted on the studied biomasses and BAs, as well as on additional and traditional for Europe and Bulgaria biomasses and BAs with potential large scale application in industry.

The summarized data reveal that Hg in BAs preferentially associates indirectly or directly with relatively stable Fe-, P-, Ti- Al-, K-, and Si-bearing minerals and phases, as well as less stable chlorides. The presence of Hg was directly identified only in K aluminosilicate (kalsilite or leucite), sylvite, and Fe oxide (probably hematite). The potential modes of Hg occurrence could be as impurities in such host matrices within BAs.

### Ecological significance of mercury in biomass and biomass ash

Mercury is a notoriously toxic element with mutagenic properties that can damage the human nervous and reproductive systems, lungs, heart, kidney, and liver, and cause vision changes, hearing defects, and loss of speech (Yudovich and Ketris, 2005b; Ariya *et al.*, 2015; Raj and Maiti, 2019; Grace Pavithra *et al.*, 2023; Wu *et al.*, 2024). Mercury from natural sources is introduced on a global scale into the atmosphere, whereas Hg from anthropogenic sources is deposited mainly locally and regionally (Gworek *et al.*, 2020). The volatile Hg enters the atmosphere and contaminates air, water, soil, and plant systems commonly as elemental Hg and, to a lesser extent, oxidized Hg<sup>2+</sup>, and particulate Hg (Yudovich and Ketris, 2005a; Yudovich and Ketris, 2005b; Lopez-Anton *et al.*, 2009; Raj and Maiti, 2019; Zhao *et al.*, 2019; Grace Pavithra *et al.*, 2023).

The contribution of Hg pollution from wastewater of coal-fired TPPs to the total Hg released to aquatic environments worldwide is estimated about 10% (Charvát *et al.*, 2020). Such data for biomass-fired TPPs are lacking. Some coal fly ash wastewaters can have higher Hg contents than the relevant limits (Zhao *et al.*, 2019). For example, the Hg toxicity limit of the US Environmental Protection Agency for drinking water is 0.002 mg l<sup>-1</sup>. The methylmercury neurotoxin species can be especially harmful to humans and wildlife (Gworek *et al.*, 2020). For instance, consumers of marine foods and rice are subjected to dangerous levels of methyl Hg exposure levels through the food chain because this Hg form is strongly diffused by phytoplankton and zooplankton in water (Gworek *et al.*, 2020; Grace Pavithra *et al.*, 2023). The oxidized form of mercury (Hg<sup>2+</sup>) occurs when the elemental Hg

comes under the influence of oxidizing conditions and this inorganic form of Hg is then methylated in aquatic systems to methyl Hg. In contrast to the elemental Hg, methylmercury is readily bioavailable (Raj and Maiti, 2019; Grace Pavithra *et al.*, 2023). The oxidized Hg is commonly water-soluble (Arvelakis *et al.*, 2010) and markedly sensitive to pH as the alkalinity decreases its mobility (Izquierdo and Querol, 2012). It can be seen that the BAs studied herein have very low Hg concentrations (0.0032–0.0452 ppm, mean 0.0225 ppm) and alkaline character (Table 2). Hence, their alkalinity can decrease Hg mobility in such environment and the biotransformation of Hg compounds to methylated species is unlikely (Pöykiö *et al.*, 2009). Hence, water treatment of BA poor in Hg (Table 2) should not provoke significant environmental concern. For example, bottom ashes and fly ashes from eucalyptus and pine barks show low Hg concentrations in the aqueous eluates (<12.1 ppb) and no specific pattern of the ecotoxicity levels were found in them (Barbosa *et al.*, 2013). Some concerns were only reported for landfill ashes produced from the incineration of municipal solid wastes because they can contain up to 70 ppm of Hg (Pöykiö *et al.*, 2009).

The high Hg concentrations in the soil inhibit plant growth due to reduced photosynthesis and absorption of minerals and nutrients (Raj and Maiti, 2019). There are data for Hg contamination of soils near coal-fired TPPs. For instance, very high Hg contents (0.34–0.75 ppm) in soils near Novocherkassk TPP in Russia burning Donbass coal were reported in the literature (Yudovich and Ketris, 2005c). However, it was stated that the major source of Hg comes from air pollution with Hg<sup>0</sup> in plant leaves and not from soil contamination because Hg-hyperaccumulating plants are rare (Gworek *et al.*, 2020). An extraordinarily high concentration of Hg (300 ppm) has been reported only in plant ash overlying Hg ore (Cohen and Dunn, 2004). Clearly, the low Hg intake by plants from the soil is beneficial for food production. In some countries, certain limits were set for Hg contents in BA (0.5–1.5 ppm) for non-problematic application to soil as fertilizer or improvement (Nzihou and Stanmore, 2013). The eight BAs studied have much lower Hg concentrations than the above limits (Table 2).

Diverse and costly pre-combustion, combustion or post-combustion Hg cleaning technologies have been applied during coal utilization with variable success (Yudovich and Ketris, 2005b; Yudovich and Ketris, 2005c; Raj and Maiti, 2019; Zhao *et al.*, 2019; Ishag *et al.*, 2022; Grace Pavithra *et al.*, 2023). However, the best approach to reduce Hg

emissions remains burning fuels with the lowest Hg contents, because the low Hg concentration in the feed fuel result in low Hg emissions and low Hg content in ash (Yudovich and Ketris, 2005b; Hower *et al.*, 2017). The upper toxicity threshold for Hg concentration in feed fuels is not established and Hg contents such as  $\leq 0.1$ , 0.5, 1 ppm and even higher have been proposed (Yudovich and Ketris, 2005b; Nunez *et al.*, 2012). In this regard, biomass with Hg  $\leq 0.1$  ppm is suitable for producing biofuel pellets, considering some European standards (Nunez *et al.*, 2012). No indications were also found that Hg contents (0.01–0.04 ppm) in diverse biomasses in the USA can exceed the Hg toxicity limit (0.2 ppm) for solid hazardous waste listed by the US Environmental Protection Agency (Thy and Jenkins, 2010). The eight biomasses and their BAs studied herein have much lower Hg concentrations than the above limits (Table 2). The reference data also show that typical solid biofuels such as various woods, miscanthus, and wheat straw also typically contain much lower Hg contents (0.009–0.01 ppm) (Van der Drift and Olsen, 1999; Cohen and Dunn, 2004; Richaud *et al.*, 2004) than coals (Table 1). Hence, the partial or complete substitution of coal by traditional biomass can reduce Hg emissions from TPPs, despite the fact that Hg in biomass also has high volatilization behaviour, commonly  $>90\%$  (Cohen and Dunn, 2004; Thy and Jenkins, 2010; Dziok *et al.*, 2020). Additionally, BA is normally enriched in some alkaline-earth and alkaline oxyhydroxides, carbonates, sulphates, and chlorides plus char, which are favourable sorbents for the sequestration of Hg and other contaminants during biomass combustion. Hence, BA also has an extra capture and storage potential for atmospheric  $\text{CO}_2$  (and probably Hg) due to the post-combustion carbonation of the oxyhydroxides by air and moisture during storage and weathering of BA (Vassilev *et al.*, 2021, 2022). These observations are also in agreement with the concept of “self-cleaning fuels” (Vassilev *et al.*, 2001, 2009).

A recent review about the content, modes of occurrence, and significance of Hg in 9 coal types and their fly ashes from 12 Bulgarian TPPs was conducted (Vassilev and Vassileva 2023). The summarized data therein show that these coals are enriched in Hg (0.14–0.57 ppm) compared with the Hg Clarke value (0.10 ppm) and the dominant quantity (50–98%) from the fuel Hg was not captured by the coal ashes. Another recent study shows that the Hg contents in the Pernik coals are also in the above listed range, namely 0.15–0.39 ppm (Yossifova *et al.*, 2024). Additionally, it was identified that the Hg concentrations in water leachates from Bulgarian

coal fly ashes (Vassilev and Vassileva, 2023) are significantly higher (0.0002–0.0013  $\text{mg l}^{-1}$ ) in comparison with the Hg Clarke values for surface water (0.00008  $\text{mg l}^{-1}$ ), but lower than the Hg toxicity limit of the US Environmental Protection Agency for drinking water (0.002  $\text{mg l}^{-1}$ ) and belong to inert wastes for landfilling according to the waste acceptance criteria for the Hg content in water leachates (0.01  $\text{mg l}^{-1}$ ) based on RD 2003/33/EC. Hence, coals and fly ashes from Bulgarian TPPs provoke certain environmental risks. In contrast, our own data show that Hg contents in the eight studied biomasses (0.003–0.043 ppm, mean 0.013 ppm) are several orders of magnitude more depleted in Hg than in Bulgarian coals. Another study on Hg contents in Bulgarian biomasses such as wheat ears, stems and leaves, as well as sunflower heads, stems and leaves shows Hg contents in the range  $<0.001$ –0.008 ppm (Yossifova and Dimitrova, 2013). These Hg values are lower or similar to our results. Hence, alternative renewable and C-neutral solid fuels poor in Hg as appropriate sustainable biomasses can be proposed to substitute partially or totally the industrial coals used in Bulgarian TPPs to minimize the Hg problems. For that reason, traditional for Bulgaria and Europe sustainable biomass resources from the second biofuel generation and their BAs will be additionally studied for contents, modes of occurrence, and behaviour of Hg during biomass combustion. Our preliminary results (Vassilev *et al.*, 2024a) on such sustainable biomasses (sunflower stalks, corn stalks, wheat straw, and sunflower and rapeseed cakes) show that they are even more perspective than the eight solid biofuels studied herein, because the Hg contents in them are lower (0.001–0.018 ppm, mean 0.007 ppm). Finally, an industrial Bulgarian fly ash produced from sunflower shells reveals very low Hg concentrations (0.021 ppm). The above results clearly show that the utilization of traditional, sustainable, renewable and C-neutral biomass as an alternative of coal can replace the costly pre-combustion, combustion or post-combustion cleaning technologies for Hg. Nevertheless, it seems that the behaviour of Hg for each biomass type needs to be studied on a case-by-case basis due to the diverse contents, modes of occurrence, and behaviour of Hg in solid biofuels and their combustion products.

## CONCLUSIONS

The content, association and potential modes of occurrence of Hg in diverse biomass ashes produced from rice husks, switchgrass, beech wood chips,

walnut shells, marine macroalgae, sunflower shells, corn cobs, and plum pits, as well as behaviour of Hg during their combustion show that:

(1) Mercury contents in the biomass ashes produced at 500 °C vary between 0.0032 and 0.0452 ppm (mean 0.0225 ppm), which are orders of magnitude lower than the Clarke value for coal ash (0.75 ppm). The varying Hg concentrations depend mostly on type, composition and origin of biomass ashes.

(2) About 60–99% (mean 87%) and 63–100% (mean 91%) of Hg in biomass were volatilized at 500 °C and 700 °C, respectively, and only limited amounts of Hg were captured by particular BAs enriched in salts such as carbonates, oxyhydroxides, phosphates, sulphates, and chlorides.

(3) Mercury in BAs preferentially associates indirectly or directly with relatively stable Fe-, P-, Ti-Al-, K-, and Si-bearing minerals and phases, as well as less stable chlorides. These associations indicate that the unstable and volatile forms of Hg in biomass shift to relatively more stable Hg-containing minerals and phases that partly captured Hg in BA.

(4) The presence of Hg in BA was only identified in K aluminosilicate (kalsilite or leucite),ylvite, and Fe oxide (probably hematite). The potential modes of Hg occurrence could be as impurities in such host matrices of BA.

(5) Alternative renewable and C-neutral solid fuels poor in Hg such as appropriate sustainable biomasses (with 0.001–0.043 ppm of Hg) are suggested to substitute partially or completely the industrial coals enriched in Hg (0.14–0.57 ppm) and used in Bulgarian TPPs to minimize environmental problems.

Future studies about the content, association, and modes of occurrence of Hg in these biomasses and biomass ashes will be conducted on the present biofuels, as well as on additional and traditional for Europe and Bulgaria biomass resources that have the potential to substitute coals in TPPs.

## Acknowledgements

This work was supported by the Bulgarian National Science Fund (grant agreement BG-175467353-2022-04-0003) and National Centre for Mechatronics and Clean Technology (grant agreement BG-05M2OP001-1.001-0008). The authors thank to prof. J. Kortenski and an anonymous reviewer for their positive evaluation and useful suggestions.

## Appendix – Nomenclature

BA – biomass ash  
BC – beech wood chips  
BCA – beech wood chips ash  
CC – corn cobs  
CCA – corn cobs ash  
DWR – dry water-soluble residue  
EDX – energy dispersive X-ray analysis  
ICP – inductively coupled plasma  
LA – laser ablation  
MM – marine macroalgae  
MMA – marine macroalgae ash  
MS – mass spectrometry  
PP – plum pits  
PPA – plum pits ash  
Ppb – part per billion  
Ppm – part per million  
RH – rice husks  
RHA – rice husks ash  
SEM – scanning electron microscopy  
SG – switchgrass  
SGA – switchgrass ash  
SS – sunflower shells  
SSA – sunflower shells ash  
TPP – thermoelectric power plant  
WS – walnut shells  
WSA – walnut shells ash  
XRD – powder X-ray diffraction  
% – weight %

## REFERENCES

- Ariya, P.A., Amyot, M., Dastoor, A., Deeds, D., Feinberg, A., Kos, G., Poulain, A., Ryjkov, A., Semeniuk, K., Subir, M., Toyota, K. 2015. Mercury physicochemical and biogeochemical transformation in the atmosphere and at atmospheric interfaces: A review and future directions. *Chemical Reviews* 115 (10), 3760–3802, <https://doi.org/10.1021/cr500667e>.
- Arvelakis, S., Crocker, C., Folkedahl, B., Pavlish, J., Spliethoff, H. 2010. Activated carbon from biomass for Mercury capture: Effect of the leaching pretreatment on the capture efficiency. *Energy and Fuels* 24 (8), 4445–4453, <https://doi.org/10.1021/ef900613b>.
- Barbosa, R., Dias, D., Lapa, N., Lopes, H., Mendes, B. 2013. Chemical and ecotoxicological properties of size fractionated biomass ashes. *Fuel Processing Technology* 109, 124–132, <https://doi.org/10.1016/j.fuproc.2012.09.048>.
- Beus, A., Grigorian, C. 1975. *Geochemical methods of prospecting and exploration of solid mineral resource deposits*. Moscow, Nedra, 279 pp. (in Russian).
- Bowen, H. 1966. *Trace elements in biochemistry*. New York, Academic Press, 241 pp.
- Cenni, R., Janisch, B., Spliethoff, H., Hein, K.R.G. 2001. Legislative and environmental issues on the use of ash from



- coal and municipal sewage sludge co-firing as construction material. *Waste Management* 21 (1), 17–31, [https://doi.org/10.1016/S0956-053X\(00\)00074-X](https://doi.org/10.1016/S0956-053X(00)00074-X).
- Charvát, P., Klimeš, L., Pospíšil, J., Klemeš, J.J., Varbanov, P.S. 2020. An overview of mercury emissions in the energy industry - A step to mercury footprint assessment. *Journal of Cleaner Production* 267, 122087, 1–11, <https://doi.org/10.1016/j.jclepro.2020.122087>.
- Chiarantini, L., Rimondi, V., Bardelli, F., Benvenuti, M., Cosio, C., Costagliola, P., Di Benedetto, F., Lattanzi, P., Saret, G. 2017. Mercury speciation in *Pinus nigra* barks from Monte Amiata (Italy): An X-ray absorption spectroscopy study. *Environmental Pollution* 227, 83–88, <https://doi.org/10.1016/j.envpol.2017.04.038>.
- Cohen, D., Dunn, C.E. 2004. *Form and distribution of trace elements in biomass for power generation*. Research Report 48 of the Cooperative Research Centre for Coal in Sustainable Development, University of New South Wales, QCAT Technology Transfer Centre, Technology Court Pullenvale, Australia, 66 pp.
- Dare, P., Gifford, J., Hooper, R.J., Clemens, A.H., Damiano, L.F., Gong, D., Matheson, T.W. 2001. Combustion performance of biomass residue and purpose grown species. *Biomass and Bioenergy* 21 (4), 277–287, [https://doi.org/10.1016/S0961-9534\(01\)00039-3](https://doi.org/10.1016/S0961-9534(01)00039-3).
- Demirbaş, A. 2003. Trace metal concentrations in ashes from various types of biomass species. *Energy Sources* 25 (7), 743–751, <https://doi.org/10.1080/00908310390212435>.
- Dziok, T., Kołodziejska, E.K., Kołodziejska, E.L. 2020. Mercury content in woody biomass and its removal in the torrefaction process. *Biomass and Bioenergy* 143, 105832, 1–7, <https://doi.org/10.1016/j.biombioe.2020.105832>.
- Erickson, J.A., Gustin, M.S., Schorran, D.E., Johnson, D.W., Lindberg, S.E., Coleman, J.S. 2003. Accumulation of atmospheric mercury in forest foliage. *Atmospheric Environment* 37 (12), 1613–1622, [https://doi.org/10.1016/S1352-2310\(03\)00008-6](https://doi.org/10.1016/S1352-2310(03)00008-6).
- Fitzgerald, W.F., Lamborg, C.H. 2014. 11.4 – Geochemistry of mercury in the environment. *Treatise on Geochemistry* 11, 91–129, <https://doi.org/10.1016/B978-0-08-095975-7.00904-9>.
- Friedli, H.R., Arellano, A.F., Cinnirella, S., Pirrone, N. 2009. Initial estimates of mercury emissions to the atmosphere from global biomass burning. *Environmental Science and Technology* 43 (10), 3507–3513, <https://doi.org/10.1021/es802703g>.
- Friedli, H.R., Radke, L.F., Lu, J.Y., Banic, C.M., Leitch, W.R., MacPherson, J.I. 2003. Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements. *Atmospheric Environment* 37 (2), 253–267, [https://doi.org/10.1016/S1352-2310\(02\)00819-1](https://doi.org/10.1016/S1352-2310(02)00819-1).
- Fytli, D., Zabaniotou, A. 2008. Utilization of sewage sludge in EU application of old and new methods – A review. *Renewable and Sustainable Energy Reviews* 12 (1), 116–140, <https://doi.org/10.1016/j.rser.2006.05.014>.
- Georgiev, S.V., Bidzhova, L. 2023. Mercury in geological materials from Bulgaria: Significance, applications, new analytical capabilities, and initial results. *Review of the Bulgarian Geological Society* 84 (3), 93–96, <https://doi.org/10.52215/rev.bgs.2023.84.3.93>.
- Grace Pavithra, K., Sundar Rajan, P., Senthil Kumar, P., Rangasamy, G. 2023. Mercury sources, contaminations, mercury cycle, detection and treatment techniques: A review. *Chemosphere* 312 (Part 1), 137314, 1–14, <https://doi.org/10.1016/j.chemosphere.2022.137314>.
- Gworek, B., Dmuchowski, W., Baczeńska-Dąbrowska, A.H. 2020. Mercury in the terrestrial environment: A review. *Environmental Science Europe* 32, 128, 1–19, <https://doi.org/10.1186/s12302-020-00401-x>.
- Hower, J.C., Clack, H.L., Hood, M.M., Hopps, S.G., Thomas, G.H. 2017. Impact of coal source changes on mercury content in fly ash: Examples from a Kentucky power plant. *International Journal of Coal Geology* 170, 2–6, <https://doi.org/10.1016/j.coal.2016.10.007>.
- Hower, J.C., Senior, C.L., Suuberg, E.M., Hurt, R.H., Wilcox, J.L., Olson, E.S. 2010. Mercury capture by native fly ash carbons in coal-fired power plants. *Progress in Energy and Combustion Science* 36 (4), 510–529, <https://doi.org/10.1016/j.peccs.2009.12.003>.
- Huang, J., Hopke, P.K., Choi, H.-D., Laing, J.R., Cui, H., Zanski, T.J., Chandrasekaran, S.R., Rattigan, O.V., Holsen, T.M. 2011. Mercury (Hg) emissions from domestic biomass combustion for space heating. *Chemosphere* 84 (11), 1694–1699, <https://doi.org/10.1016/j.chemosphere.2011.04.078>.
- Ishag, A., Yue, Y., Xiao, J., Huang, X., Sun, Y. 2022. Recent advances on the adsorption and oxidation of mercury from coal-fired flue gas: A review. *Journal of Cleaner Production* 367, 133111, 1–13, <https://doi.org/10.1016/j.jclepro.2022.133111>.
- Izquierdo, M., Querol, X. 2012. Leaching behaviour of elements from coal combustion fly ash: An overview. *International Journal of Coal Geology* 94, 54–66, <https://doi.org/10.1016/j.coal.2011.10.006>.
- Ketris, M.P., Yudovich, Y.E. 2009. Estimations of Clarkes for carbonaceous biolithes: World averages for trace element contents in black shales and coals. *International Journal of Coal Geology* 78 (2), 135–148, <https://doi.org/10.1016/j.coal.2009.01.002>.
- Kolker, A., Senior, C.L., Quick, J.C. 2006. Mercury in coal and the impact of coal quality on mercury emissions from combustion systems. *Applied Geochemistry* 21 (11), 1821–1836, <https://doi.org/10.1016/j.apgeochem.2006.08.001>.
- Kostova, I. 2017. Abundance, distribution and mode of occurrence of mercury in Bulgarian low to medium-sulphur coals. *Comptes rendus de l'Academie bulgare des Sciences* 70 (9), 1279–1288.
- Kostova, I., Vassileva, C., Dai, S., Hower, J.C. 2016. Mineralogy, geochemistry and mercury content characterization of fly ashes from the Maritza 3 and Varna thermoelectric power plants, Bulgaria. *Fuel* 186, 674–684, <https://doi.org/10.1016/j.fuel.2016.09.015>.
- Lei, Z., Pavia, S., Wang, X. 2024. Biomass ash waste from agricultural residues: Characterisation, reactivity and potential to develop one-part geopolymer cement. *Construction and Building Materials* 431, 136544, 1–12, <https://doi.org/10.1016/j.conbuildmat.2024.136544>.
- Lopez-Anton, M.A., Abad-Valle, P., Diaz-Somoano, M., Martinez-Tarazona, M.R. 2009. Evaluation of the variables that influence mercury capture in solid sorbents. *Coal Combustion and Gasification Products* 1, 32–37, <https://doi.org/10.4177/CCGP-D-09-00007.1>.
- Madsen, P.P. 1981. Peat bog records of atmospheric mercury deposition. *Nature* 293 (5828), 127–130, <https://doi.org/10.1038/293127a0>.
- Méndez-López, M., Parente-Sendín, A., Calvo-Portela, N., Gómez-Armesto, A., Eimil-Fraga, C., Alonso-Vega, F., Arias-Estévez, M., Nóvoa-Muñoz, J.C. 2023. Mercury in a birch forest in SW Europe: Deposition flux by litterfall and pools in aboveground tree biomass and soils. *Science of the Total Environment* 856 (Part 1), 158937, 1–11, <https://doi.org/10.1016/j.scitotenv.2022.158937>.

- Nanda, S., Mohanty, P., Pant, K.K., Naik, S., Kozinski, J.A., Dalai, A.K. 2013. Characterization of North American lignocellulosic biomass and biochars in terms of their candidacy for alternate renewable fuels. *BioEnergy Research* 6 (2), 663–677, <https://doi.org/10.1007/s12155-012-9281-4>.
- Nordin, A. 1994. Chemical elemental characteristics of biomass fuels. *Biomass and Bioenergy* 6 (5), 339–347, [https://doi.org/10.1016/0961-9534\(94\)E0031-M](https://doi.org/10.1016/0961-9534(94)E0031-M).
- Nunez, C.A.F., Jochum, J., Vargas, F.E.S. 2012. Characterization and feasibility of biomass fuel pellets made of Colombian timber, coconut and oil palm residues regarding European standards. *Environmental Biotechnology* 8 (2), 67–76.
- Nzihou, A., Stanmore, B. 2013. The fate of heavy metals during combustion and gasification of contaminated biomass - A brief review. *Journal of Hazardous Materials* 256–257, 56–66, <https://doi.org/10.1016/j.jhazmat.2013.02.050>.
- Pacyna, E.G., Pacyna, J.M., Sundseth, K., Munthe, J., Kindbom, K., Wilson, S., Steenhuisen, F., Maxson, P. 2010. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmospheric Environment* 44 (20), 2487–2499, <https://doi.org/10.1016/j.atmosenv.2009.06.009>.
- Perelman, A. 1989. *Geochemistry*. Vishaya Shkola, Moscow, 528 pp. (in Russian).
- Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R.B., Friedli, H.R., Leaner, J., Mason, R., Mukherjee, A.B., Stracher, G.B., Streets, D.G., Telmer, K. 2010. Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmospheric Chemistry and Physics* 10 (13), 5951–5964, <https://doi.org/10.5194/acp-10-5951-2010>.
- Pöykiö, R., Rönkkömöki, H., Nurmesniemi, H., Perämäki, P., Popov, K., Välimäki, I., Tuomi, T. 2009. Chemical and physical properties of cyclone fly ash from the grate-fired boiler incinerating forest residues at a small municipal district heating plant (6 MW). *Journal of Hazardous Materials* 162 (2–3), 1059–1064, <https://doi.org/10.1016/j.jhazmat.2008.05.140>.
- Raj, D., Maiti, S.K. 2019. Sources, toxicity, and remediation of mercury: an essence review. *Environmental Monitoring and Assessment* 191 (9), 566, 1–22, <https://doi.org/10.1007/s10661-019-7743-2>.
- Reimann, C., Koller, F., Frengstad, B., Kashulina, G., Niskavaara, H., Englmaier, P. 2001. Comparison of the element composition in several plant species and their substrate from a 1500000-km<sup>2</sup> area in Northern Europe. *Science of the Total Environment* 278 (1–3), 87–112, [https://doi.org/10.1016/S0048-9697\(00\)00890-1](https://doi.org/10.1016/S0048-9697(00)00890-1).
- Reimann, C., Ottesen, R.T., Andersson, M., Arnoldussen, A., Koller, F., Englmaier, P. 2008. Element levels in birch and spruce wood ashes – green energy? *Science of the Total Environment* 393 (2–3), 191–197, <https://doi.org/10.1016/j.scitotenv.2008.01.015>.
- Richaud, R., Herod, A.A., Kandiyoti, R. 2004. Comparison of trace element contents in low-temperature and high-temperature ash from coals and biomass. *Fuel* 83 (14–15), 2001–2012, <https://doi.org/10.1016/j.fuel.2004.05.009>.
- Ross, A.B., Jones, J.M., Chaiklangmuang, S., Pourkashanian, M., Williams, A., Kubica, K., Andersson, J.T., Kerst, M., Danihelka, P., Bartle, K.D. 2002. Measurement and prediction of the emission of pollutants from the combustion of coal and biomass in a fixed bed furnace. *Fuel* 81 (5), 571–582, [https://doi.org/10.1016/S0016-2361\(01\)00157-0](https://doi.org/10.1016/S0016-2361(01)00157-0).
- Rumayor, M., Lopez-Anton, M.A., Díaz-Somoano, M., Martínez-Tarazona, M.R. 2015. A new approach to mercury speciation in solids using a thermal desorption technique. *Fuel* 160, 525–530, <https://doi.org/10.1016/j.fuel.2015.08.028>.
- Saqib, N., Bäckström, M. 2014. Trace element partitioning in ashes from boilers firing pure wood or mixtures of solid waste with respect to fuel composition, chlorine content and temperature. *Waste Management* 34 (12), 2505–2519, <https://doi.org/10.1016/j.wasman.2014.08.025>.
- Sarabèr, A. 2012. Co-combustion and its impact on fly ash quality; pilot-scale experiments. *Fuel Processing Technology* 104, 105–114, <https://doi.org/10.1016/j.fuproc.2012.04.033>.
- Schofield, K. 2008. Fuel-mercury combustion emissions: An important heterogeneous mechanism and an overall review of its implications. *Environmental Science and Technology* 42 (24), 9014–9030, <https://doi.org/10.1021/es801440g>.
- Shah, P., Strezov, V., Nelson, P.F. 2010. Speciation of mercury in coal-fired power station flue gas. *Energy and Fuels* 24 (1), 205–212, <https://doi.org/10.1021/ef900557p>.
- Someshwar, A.V. 1996. Wood and combination wood-fired boiler ash characterization. *Journal of Environmental Quality* 25 (5), 962–972, <https://doi.org/10.2134/jeq1996.00472425002500050006x>.
- Sørum, L., Frandsen, F.J., Hustad, J.E. 2003. On the fate of heavy metals in municipal solid waste combustion. Part I: Devolatilisation of heavy metals on the grate. *Fuel* 82 (18), 2273–2283, [https://doi.org/10.1016/S0016-2361\(03\)00178-9](https://doi.org/10.1016/S0016-2361(03)00178-9).
- Strezov, V., Evans, T.J., Ziolkowski, A., Nelson, P.F. 2010. Mode of occurrence and thermal stability of mercury in coal. *Energy and Fuels* 24 (1), 53–57, <https://doi.org/10.1021/ef900473p>.
- Tamaki, Y., Mazza, G. 2010. Measurement of structural carbohydrates, lignins, and micro-components of straw and shives: Effects of extractives, particle size and crop species. *Industrial Crops and Products* 31 (3), 534–541, <https://doi.org/10.1016/j.indcrop.2010.02.004>.
- Thy, P., Jenkins, B.M. 2010. Mercury in biomass feedstock and combustion residuals. *Water, Air, and Soil Pollution* 209, 429–437, <https://doi.org/10.1007/s11270-009-0211-9>.
- Van der Drift, A., Olsen, A. 1999. *Conversion of biomass, (private) prediction and solution methods for ash agglomeration and related problems*. Project Report of ECN, Petten, The Netherlands, 89 pp.
- Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G. 2010. An overview of the chemical composition of biomass. *Fuel* 89 (5), 913–933, <https://doi.org/10.1016/j.fuel.2009.10.022>.
- Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G., Morgan, T.J. 2012. An overview of the organic and inorganic phase composition of biomass. *Fuel* 94, 1–33, <https://doi.org/10.1016/j.fuel.2011.09.030>.
- Vassilev, S.V., Baxter, D., Vassileva, C.G. 2013. An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter. *Fuel* 112, 391–449, <https://doi.org/10.1016/j.fuel.2013.05.043>.
- Vassilev, S.V., Baxter, D., Vassileva, C.G. 2014a. An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types. *Fuel* 117 (Part A), 152–183, <https://doi.org/10.1016/j.fuel.2013.09.024>.
- Vassilev, S.V., Eskenazy, G.M., Vassileva, C.G. 2001. Behaviour of elements and minerals during preparation and combustion of the Pernik coal, Bulgaria. *Fuel Processing Technology* 72 (2), 103–129, [https://doi.org/10.1016/S0378-3820\(01\)00186-2](https://doi.org/10.1016/S0378-3820(01)00186-2).
- Vassilev, S.V., Vassileva, C.G. 2019. Water-soluble fractions of biomass and biomass ash and their significance for biofuel

- application. *Energy and Fuels* 33 (4), 2763–2777, <https://doi.org/10.1021/acs.energyfuels.9b00081>.
- Vassilev, S.V., Vassileva, C.G. 2023. A retrospection on the content, association, and significance of mercury in coals and coal ashes from Bulgarian thermoelectric power stations. *Journal of Hazardous Materials* 457, 131850, 1–8, <https://doi.org/10.1016/j.jhazmat.2023.131850>.
- Vassilev, S.V., Vassileva, C.G., Baxter, D. 2014b. Trace element concentrations and associations in some biomass ashes. *Fuel* 129, 292–313, <https://doi.org/10.1016/j.fuel.2014.04.001>.
- Vassilev, S.V., Vassileva, C.G., Baxter, D., Andersen, L.K. 2009. A new approach for the combined chemical and mineral classification of the inorganic matter in coal. 2. Potential applications of the classification systems. *Fuel* 88 (2), 246–254, <https://doi.org/10.1016/j.fuel.2008.09.005>.
- Vassilev, S.V., Vassileva, C.G., Georgieva, M.G., Barbov, B.Z., Velyanova, G.G., Georgiev, S.V. 2024a. Content, association and potential modes of occurrence of mercury in diverse biomass types and their ecological significance. *Geologica Balcanica* 53 (2), 69–87, <https://doi.org/10.52321/GeolBalc.53.2.69>.
- Vassilev, S., Vassileva, C., Georgieva, M., Velyanova, G., Bidzhova, L., Georgiev, S. 2024b. Behavior of mercury during biomass combustion. *Review of the Bulgarian Geological Society* 85 (3), 178–181, <https://doi.org/10.52215/rev.bgs.2024.85.3.178>.
- Vassilev, S.V., Vassileva, C.G., Petrova, N.L. 2021. Mineral carbonation of biomass ashes in relation to their CO<sub>2</sub> capture and storage potential. *ACS Omega* 6 (22), 14598–14611, <https://doi.org/10.1021/acsomega.1c01730>.
- Vassilev, S.V., Vassileva, C.G., Petrova, N.L. 2022. Mineral carbonation of thermally treated and weathered biomass ashes with respect to their CO<sub>2</sub> capture and storage. *Fuel* 321, 124010, 1–11, <https://doi.org/10.1016/j.fuel.2022.124010>.
- Vassilev, S.V., Vassileva, C.G., Song, Y.-C., Li, W.-Y., Feng, J. 2017. Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion. *Fuel* 208, 377–409, <https://doi.org/10.1016/j.fuel.2017.07.036>.
- Vinogradov, A. 1962. Average element contents of major types magmatic rocks in Earth crust. *Geochimica* 7, 555–572 (in Russian).
- Wiinikka, H., Grönberg, C., Boman, C. 2013. Emissions of heavy metals during fixed-bed combustion of six biomass fuels. *Energy and Fuels* 27 (2), 1073–1080, <https://doi.org/10.1021/ef3011146>.
- Wu, Y.-S., Osman, A.I., Hosny, M., Elgarahy, A.M., Elta- weil, A.S., Rooney, D.W., Chen, Z., Rahim, N.S., Sekar, M., Gopinath, S.C.B., Rani, N.N.I.M., Batumalaie, K., Yap, P.-S. 2024. The toxicity of mercury and its chemical compounds: molecular mechanisms and environmental and human health implications: A comprehensive review. *ACS Omega* 9 (5), 5100–5126, <https://doi.org/10.1021/acsomega.3c07047>.
- Xu, Z., Wang, Z., Niu, X., Tao, J., Fan, M., Wang, B., Zhang, M., Zhang, X. 2023. High-resolution atmospheric mercury emission from open biomass burning in China: Integration of localized emission factors and multi-source finer resolution remote sensing data. *Environment International* 178, 108102, 1–8, <https://doi.org/10.1016/j.envint.2023.108102>.
- Yossifova, M., Dimitrova, D. 2013. Trace elements in some biomass collected from areas associated with the lignite mining and power producing enterprise Maritsa East, Bulgaria. *Geologica Balcanica* 42 (1–3), 49–57, <https://doi.org/10.52321/GeolBalc.42.1-3.49>.
- Yossifova, M., Dimitrova, D., Bidzhova, L., Veleva, O., Georgiev, S.V. 2024. Mercury contents in Pernik coals and disposal pond waste products. *Review of the Bulgarian Geological Society* 85 (2), 207–210, <https://doi.org/10.52215/rev.bgs.2024.85.2.207>.
- Yudovich, Y.E., Ketris, M.P. 2005a. Mercury in coal: a review. Part 1. Geochemistry. *International Journal of Coal Geology* 62 (3), 107–134, <https://doi.org/10.1016/j.coal.2004.11.002>.
- Yudovich, Y.E., Ketris, M.P. 2005b. Mercury in coal: a review. Part 2. Coal use and environmental problems. *International Journal of Coal Geology* 62 (3), 135–165, <https://doi.org/10.1016/j.coal.2004.11.003>.
- Yudovich, Y.E., Ketris, M.P. 2005c. *Toxic trace elements in coal*. Ekaterinburg, Ural Division, RAS, 656 pp. (in Russian).
- Zhao, S., Pudasainee, D., Duan, Y., Gupta, R., Liu, M., Lu, J. 2019. A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies. *Progress in Energy and Combustion Science* 73, 26–64, <https://doi.org/10.1016/j.pecc.2019.02.001>.