Article

An Influence of the Fuel Type on Element Behaviour in Domestic Boilers with Respect to the Circular Economy

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Abstract: The use of waste from the regional production of waste wood, waste paper, and cardboard in the form of briquettes may be causing an increase in local emissions, both of major elements and trace elements. When burning paper and cardboard briquettes, more than 70% of Mn, Zn, As, and Pb is released into the air from the total content of trace elements in the fuel. The largest amounts of major and trace elements are released when burning paper briquettes (56 g/kg of fuel); half of these amounts are released from burning briquettes from waste wood and coal (23 g/kg of fuel). The pursuit of alternative uses for those cardboard components that are not suitable for recycling cannot be directed to the production of briquettes for residential combustion in the framework of the application of the principles of the circular economy. In particular, the high concentrations of undesirable elements in the emissions released in the gas phase into the atmosphere are an obstacle existing even when the parameters of the PM₁₀ emissions of a boiler are met. This is related to the high ash content of the cardboard (13.5%). Waste paper or cardboard could be added to waste wood at a maximum of 10% to make the pollution produced comparable to the burning of coal briquettes.

Keywords: waste paper; cardboard; waste wood; coal; ash; residential wood combustion

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1. Introduction

The use of biomass as renewable, carbon-neutral fuel for heat and electric energy is strongly supported in the EU. This support has triggered a sharp increase in the use of wood, which increases every year [1]. The rapid development of residential wood combustion (RWC) is linked to the positive image of wood as domestic and renewable fuel [2]. Increasing pressure to limit the European biomass market requires compliance with the conditions for its sustainable utilisation. This suggests that the future cost of biomass will change depending on many factors: local conditions, resource availability, and sustainability criteria [3]. A non-questionable role will be played by improving the use of waste biomass within the circular economy. The wood industry and many governments promote the utilisation of wood, while many environmental groups oppose wood bioenergy because it causes deforestation, which harms natural carbon sinks, ecosystems, and biodiversity [4]. The pros and cons of using wood waste as a source of heat and energy within the circular economy are explained by Millward-Hopkins and Purnel [5].

Residential wood combustion (RWC) is an important contributor to air quality in numerous regions worldwide. In central and eastern Europe, the contribution from RWC

is estimated at 32% of the total PM_{2.5} concentration [6], up to 45% of RWC's PM_{2.5} [7]. Annual average fractions of PM_{2.5} concentrations attributed to RWC form up to 70% (Oslo), equivalent to 7.8 mg/m³ [6]. The contribution of wood smoke to ambient PM was highly dependent on seasonality, the density of sources, specific technologies used, meteorology, and topography [8]. The most important pollutants include CO, particulate matter (PM), elemental carbon (EC), organic carbon (OC), polyaromatic hydrocarbons [9] and heavy metals—Pb, Cu, Fe, Zn, Hg, and others [6]. Emitted OC is converted by atmospheric oxidation to a secondary organic aerosol [8].

Even a relatively “clean fuel” can produce significant pollution, which is mainly affected by an inappropriate fuel burning rate and poorly mixed ratios between fuel and air. Older boilers are known to produce higher dust emission loads than modern boiler types. The pollution produced by traditional logwood boilers is 5–10 times (different for each pollutant) higher than in the case of modern logwood boilers and pellet boilers [10]. Emission factors, which are key indicators in terms of emission control strategies, are used to estimate the emission burden from domestic boilers.

The literature references state that particle emission factors from residential biomass combustion may show wide variation due to the type of biomass burned, the characteristics of combustion facility, and burning rate [11,12]. In addition to the technical parameters of the boiler and the combustion conditions, the emission of dust particles is significantly influenced by the fuel type (wood logs, chips, pellet, briquettes) and also for new kinds of biofuel made from residues from other activities, such as forestry or the furniture industry [13]. The use of waste wood and other biomass products is particularly encouraged by the circular economy.

In an overloaded boiler of older production, emissions from burning wood biomass increase 2–6 times, while moist fuel increases emissions 1.5 to 2 times. In modern boilers, PM_{2.5} emissions are increased 8–10 times using higher humidity fuel due to the limited capacity of the air systems [10]. By burning too-dry fuel at a high load, modern boilers increase their PM_{2.5} emissions 4–5 times compared to a nominal load and standard fuel.

At the present time, emission factors (EF) for fine inhalable particles, with diameters that are generally 2.5 micrometres and smaller than PM_{2.5}, are being monitored. Older published data reported the emission factor for dust particles (without size limitation). The difference between the emission factors for dust particles and PM_{2.5} particles was observed by Shen et al. [9]. The emission factor values for PM from logwood combustion are in the range of 0.71–6.2 g/kg with an average value of 2.1 ± 1.3 g/kg, and for PM_{2.5} particles, they are in the almost identical range of 0.5–6.0 g/kg with an average value of 1.8 ± 1.3 g/kg.

Measurements from Norway, where the highest wood stove emissions factor for birch and spruce was found to be 36 g/kg [14], demonstrate a high variability of emission factors when burning wood biomass. Under standard conditions and at a steady state (nominal load), the emissions from the combustion of PM_{2.5} reach up to 84 mg/MJ (1.34 g/kg of fuel for 16 MJ/kg in gross calorific value). This value increased to 105 mg/MJ when the ignition phase is included in the measurement. During burning wet log fuelwood, the value increases by 27% to 568 mg/MJ [10].

Differing values of emission factors have been published. For example, according to the EMEP/EEA Guidebook [15], the emission factor ranges are as follows: for modern boilers (advanced or eco-labelled) the PM_{2.5} average value is 93 mg/MJ ranging from 19 to 33 mg/MJ, for traditional boilers 470 (235–940) mg/MJ, pellet boilers 29 (9–47) mg/MJ, and for older boilers 740 (370–1480) mg/MJ, equivalent to approximately 23.6 g/kg of fuel with a gross calorific value of 16 MJ/kg [15]. For old boilers, Klimont et al. [16] report an even higher emission factor value for dust particles (73–2200 mg/MJ). The PM emission factor is significantly higher in briquette combustion than with fuelwood, the value of which is 7.76 ± 6.02 g/kg [17].

The PM emission factor for the combustion of bituminous coal briquettes ranges from 0.17–26 g/kg to 0.13 g/kg for PM_{2.5}. When burning bituminous coal briquettes,

more significant differences were found for the average emission factor value for PM (3.5 ± 6.5 g/kg) and for PM_{2.5} 7.7 ± 5.8 g/kg [9]. A substantially higher emission factor for bituminous coal (14.4 g/kg) is reported by Butcher and Ellenbecker [11]. The EF value for anthracite coal was reported to be only 0.5 g/kg, which is related to a low volatile flammable substance content and a high fixed carbon content, which stabilised combustion during the heating period [18].

The EF PM_{2.5} values for old boilers indicate that the amounts of particles produced may be higher during burning biomass than when burning bituminous coal [9,16]. Emission factors represent a significant step for an objective comparison of the technical parameters of the combustion equipment for standardised fuels. When burning biomass, some elements go into a gaseous phase depending on the combustion temperature; therefore, they are not included in the EF. The resulting environmental load of burning biomass will be higher.

During wood combustion, 85–100% of Cl and approximately 50–70% of S are already released at 500 °C into the gaseous phase [19]. The release of Na, K, Zn, and Pb is influenced by the type of biomass and temperature. Zn and Pb start to be released at 500 °C, and at 850 °C, more than 65–85% of the total element content is released into the air [20]. When burning biomass, amounts of trace elements are released in the following order: As > Cd, Pb, Zn > Cu [20]. Of the major elements, 70–90% of K and Na are released at a higher temperature (800–1050 °C) [19]. At 1000 °C, 94 to 99% of K and 97–99% of Na are released depending on the original concentration of the element in biomass [21]. The release of Si and Ca into the gas phase in smaller quantities than K and S is reported by Trojanowski and Fthenakis [7]. Burning biomass, especially waste biomass (mixture of waste from furniture production and wood waste) or waste cardboard, can cause a higher environmental load than burning fossil fuels.

The article aims to compare the amounts of released major and trace elements during the combustion of fuels prepared from waste biomass and fossil fuels and highlight the dangers associated with the presence of harmful substances released into the atmosphere. These problems are particularly significant in using waste wood as a small part of biomass fuel because protective chemical compounds (pesticides, fire retardants) or dyes, inks, and additives used to modify the properties of paper are important sources of trace elements. The importance of this research is linked to the “pressure” to secure cheaper fuels and meet the objectives of the circular economy—using waste as a potential raw material. Studying the behaviour of major and trace elements was also aimed at monitoring the possibility of using deposits in the flue duct to identify the burned fuel.

2. Material and Methods

2.1. Material

Three types of fuels were used (fossil fuel and two types of biomass) of approximately “same shape”—briquettes (Table 1).

Table 1. Proximate and ultimate analysis of combusted fuels in dry matter.

Fuel	Moisture	VM	FC	Ash	C	H	N	S	O	GCV
					%					MJ/kg
CB										
REKORD 7	max 19	50.61	42.89	5.50	58.97	4.92	0.67	<0.50	29.94	19.2
WM	max 8	75.23	23.82	0.95	46.27	5.42	1.64	0.71	44.10	17.8
PB										
(SaverBrik)	max 8	79.65	7.15	13.2	38.30	5.29	0.11	<0.10	43.30	16.1

Explanation: GCV—Gross calorific value.

Coal briquettes (CB) with the trade name “REKORD 7” come from lignite in the Lumber Range (Welzow-Süd and Nochten mines) which are further processed by Lausitz Energie Bergbau AG (LEAG) at the Schwarze Pumpe plant. The briquettes are produced without binders and are available at all fuel suppliers in the Czech Republic. The sales price plus VAT is EUR 2.67/10 kg. The advantage of CB briquettes for domestic heating is a higher fixed-carbon content.

Paper briquettes ((PB) SaverBrik POWER type RUF-P (manufacturer SaverBrik, the Czech Republic)) are produced from mixture of coarsely crushed cardboard and recovered paper using high pressure. The sales price of these briquettes ranges from 0.85 to 1.25 EUR/10 kg with VAT.

Briquettes made from waste wood from furniture production (WM) with the addition of wood-processing waste containing polymer materials—veneer, wood, wood composites, and MDF (medium-density fibrewood) products come from a plant (Ostravice, Moravian-Silesian Region, the Czech Republic) corresponding to category 1.2.3 “homogeneous mixtures and mixtures” defined by ISO 17225-7 (WM) [22]. The sales price plus VAT is EUR 2.24/10 kg. Therefore, the costs of obtaining 100 MJ are comparable for briquettes CB and WM (EUR 1.3 and EUR 1.2), while for PB, it is half the cost (EUR 0.6).

In addition to the input fuel, combustion products were analysed: ash (A)—samples taken from the bottom of the boiler and deposits (D)—samples taken from the wall of the boiler and heat exchange surface (Table 2). Char/soot terminology is used for high-carbon material in atmospheric deposition. Char retains the morphology of the source material with diameters ranging mainly from 1 to 100 μm [23]. Soot is submicron particles ($<1 \mu\text{m}$) formed from the condensation of hydrocarbon radicals at high temperature ($>600 \text{ }^\circ\text{C}$) via conversions in flue gas [24]. As the samples taken did not fit either definition (particle size, presence of a primary particle structure from the fuel), they were marked as deposits.

Table 2. Conditions for combustion experiments in EC2, EC3 boilers.

Paper Briquettes (PB)					Wood Mixture (WM)					Coal Briquettes (CB)				
Sample	D	A	FC	TC	Sample	D	A	FC	TC	Sample	D	A	FC	TC
	g/kg Fuel	kg/h	h			g/kg Fuel	kg/h	h			g/kg Fuel	kg/h	h	
EC2 134	0.55	110	3.40	9.0	EC2 128	0.81	9.37	2.93	4	EC2 51	0.40	65.1	2.86	10.5
EC2 135	0.59	107	4.70	7.5	EC2 129	0.92	9.58	2.25	3	EC2 55	0.47	67.3	2.86	10.5
EC2 146	0.51	157	6.00	8.5	EC2 130	1.18	10.94	2.25	4	EC2 58	0.41	43.0	3.71	10.5
EC2 147	0.61	134	5.20	8.5						EC2 65	0.43	52.1	3.76	10.0
EC2 AVG	0.57	127	4.83	8.38		0.97	9.96	2.48	3.67	EC2 66	0.45	55.1	3.54	10.0
EC2 STD	0.04	23.4	1.09	0.63		0.16	0.85	0.32	0.47		0.43	56.5	3.35	10.30
EC3 168	1.10	128	3.80	10.5	EC3 125	0.15	7.72	3.89	4	EC3 64	0.47	67.3	2.40	12.5
EC3 170	0.92	131	3.80	10.5	EC3 126	0.16	7.59	4.44	4	EC3 72	0.60	43.5	3.81	10.5
EC3 180	0.75	125	4.00	10.0	EC3 127	0.25	8.26	3.75	4	EC3 73	0.49	42.9	3.75	12.0
EC3 181	1.00	115	4.20	9.50						EC3 76	0.53	62.7	2.73	11.0
EC3 183	0.94	149	3.00	10.0										
EC3 AVG	0.94	129	3.77	10.10		0.19	7.86	4.03	4.00		0.52	54.1	3.17	11.5
EC3 STD	0.13	12.5	0.46	0.42		0.06	0.36	0.36	0.00		0.06	12.7	0.72	0.91

Explanation: A—Ash; AVG—Arithmetic mean; D—Deposits; FC—Fuel consumption; STD—Standard deviation; TC—Time of combustion.

2.2. Conditions of the Combustion

WM briquettes were burnt in continuous burning boilers of emission class EC2 (BEC2) and EC3 (BEC3) defined according to EN 303-5 [25]. Boilers had manual stoking.

Boilers differ in design elements: in particular, the arrangement of heat-exchanging surfaces, the intensity of the burning, or the ways of feeding primary and secondary air, the arrangement of the burn-out chamber, and the turbulence inside the combustion chamber.

The advantages of EC3 boilers, for example, are turbofans installed to allow more intense thermal decomposition and the more precise positioning of the air vents on the grate. Currently, the approximate frequencies of representation of both groups in local heating are equal.

The combustion tests were conducted at a minimum of six hours with approximately the same thermal operation. Constant marginal conditions were ensured, including, for example, heat collection, fuel grain size composition, amount and method of fuel supply, and ambient temperature. The walls of the EC3 boiler are lined with a chamotte lining to help maintain a higher temperature in the boiler. Information on the amount of burned fuel, sediment production, and ash are given in Table 2.

Six combustion tests were carried out with WM briquettes, three for each boiler. PB briquettes were burned ten times (five times in the EC2 boiler and five times in the EC3 boiler). One test for the EC2 boiler was excluded due to poor fuel burn, which was caused by a lack of air supply.

2.3. Analytical Methods

Samples of the deposits WM, PB, CB and ash from WM and PB were screened on sieves: 0.045, 0.125, 0.25, 0.50, 1.00, 2.00, and 2.50 mm (Preciselekt, Czech Republic) at the sieving machine Fritsch Analysette 3 Spartan. Ash from the combustion of CB was very coarse; therefore, 6.3- and 12.5-mm sieves were added. The weight proportions of particles for individual grain size classes were determined as a base for the calculation of the yield.

The mineralogical phase analyses of the deposits and samples were performed by X-ray diffraction (Diffractometer Bruker Advance D8) using the standard Rietveld method of quantitative phase analysis. Analysis of organic compounds in WM fuel was done by the Py-GC/MS method. Sample preparation and measurement methods are described in detail by Ruzickova et al. [26]. The other methods used are standardised, and their overview, including information on the instrumentation used, is given in Table 3.

Table 3. Overview of standardised methods used.

Matrix	Parameter	Standard/Methods	Equipment
A, D, F	Ash	ISO 18122:2015 [27]	Laboratory furnace LAC LH, Czech Republic
A, D, F	Ultimate analysis (C,H,N)	ISO 16948:2015 [28]	FleshSmart Elemental Analyser.
A, D, F	S—determination	ISO 16994:2016 [27]	Thermoscientific
F	Calorific value	ISO 18125:2017 [29]	Calorimeter AC 500, LECO, USA
A, D, F	Elemental analysis—X-ray fluorescence	U.S. EPA 2007, method 6200 [30]	Innov-X analyser, Olympus
F	Moisture	ISO 18134-2:2017 [31]	Memmert UN30, Germany
A, D	Water leachate	EN 12457-2 [32]	Overhead shaker GFL 3040, Germany
WL	Major anions (chloride)	U.S. EPA 1997, Method 300.1 [33]	Ion chromatograph 940 Professional IC Vario TWO/SeS/PP, Metrohm
F(coal), A	Grain size analysis	ASTM D293/D293M—18 [34]	Vibratory sieve shaker Analysette
F(bio), A	Grain size analysis	ISO 17827-2:2016 [35]	3 Spartan, Fritsch, Germany

Explanation: A—Ash; Bio—biomass; D—Deposit; F—Fuel, WL—Water leachate.

3. Results

3.1. Basic Information about the Burning Process

The amounts of ash obtained by burning 1 kg of fuel in BEC2 and BEC3 are approximately equivalent to the laboratory results of the determination of ash in fuel according to ISO 18122:2015 [27] (Table 1). Burning 1 kg of CB under laboratory conditions would yield 55 g/kg of ash, while burning in BEC2 yielded 56.5 ± 8.9 g/kg and BEC3 54.1 ± 11.0 g/kg (Figure 1). Additionally, the amounts of deposits produced were comparable for both boilers. These were 0.43 ± 0.03 g/kg for the EC2 boiler and 0.52 ± 0.05 g/kg

for the EC3 boiler (Figure 2). While burning PB under laboratory conditions produced 127 ± 23 g/kg of ash in BEC2, and 118 ± 45 g/kg of ash in the EC3 boiler, the amounts of deposits captured differed for the BEC2 and BEC3 boiler. The higher amounts of deposits were collected in the BEC3 boiler (0.94 ± 0.13 g/kg), while in BEC2, it was 0.57 ± 0.04 g/kg of fuel. The difference is caused by the higher uptake of inorganic particles in the BEC3 deposits ($22.7 \pm 3.84\%$) than in BEC2 ($19.5 \pm 1.73\%$), which confirmed the higher efficiency of the EC3 boiler in capturing inorganic particles resulting from the condensation of the gaseous component. The biggest difference is shown in the results obtained by burning WM when substantially smaller amounts of ash were produced. In BEC3, the amount of ash obtained (7.86 ± 0.29 g/kg of fuel) was lower than the ash determined according to ISO 18122:2015 [27] (9.5 g/kg of fuel).

Figure 1. Amounts of ash (a) and deposits (b) formed by the combustion of 1 kg of fuel.

Figure 2. Amounts of inorganic component (ash) in deposits (a) and amounts of unburned carbon in deposits (b).

In this case, when the content of inorganic elements in the input fuel is minimal, the amounts of deposits captured in BEC3 is lower (0.19 ± 0.04 g/kg of fuel) than in BEC2 (0.97 ± 0.16 g/kg of fuel). As a result, only $13.82 \pm 1.21\%$ of the inorganic component was captured in the deposits from BEC3, compared to $21.81 \pm 1.05\%$ in BEC2. When burning in BEC2, the temperature was probably lower, which did not allow further thermal decomposition of the major mineral phase of Ca (calcite). The X-ray diffraction method determined the calcite content in deposits from BEC2 $10.56 \pm 2.02\%$ and in deposits from BEC3 $3.58 \pm 0.64\%$ (normalised to 100%). In the deposits from the EC3 boiler,

1.69% of Ca is in the form of calcite, which corresponds to 31% of the total Ca bound in the crystalline phase. In the deposits from the EC2 boiler, 4.75% of Ca is bound in the crystalline phase, which is equivalent to 54.5% of the total Ca content in the deposit. The higher temperature in the EC3 boiler was confirmed by the predominant amorphous character of the deposit particles.

3.2. The Form of Occurrence of Elements in Fuels

3.2.1. Waste Paper and Cardboard

The high fibre plant material content and low ash content of the waste paper are interesting in terms of its further energy use. Corrugated cardboard contains up to 95% of organic matter, while printing paper contains 70–100% of organic matter and 0–30% of inorganic matter. The chemical composition of the paper depends on the type or grade of the paper. Paper is a heterogeneous mixture of fibre plant material—mostly cellulose, hemicellulose and, in smaller quantities, lignin or various compounds of lignin (Na-lignate) and inorganic compounds (filler). The fibre in newsprint is composed of 45.6% cellulose, 31.3% hemicellulose, and 23.1% lignin [36]. In paper production, to improve surface characteristics of paper, the following chemical compounds are used as precipitators and stabilizers: aluminium sulphate, aluminium chloride hydroxide, aluminium formiate, aluminium nitrate, and sodium aluminium components [37].

A significant component of the paper is coating pigments (4%) and chemical additives (3–8%), whose use depends on the grade of the paper [38]. Printing is also the source of trace elements in waste paper. The main components of the inks are colouring substances (5–30%), binders (15–50%), solvents (15–65%), and additives (1–10%). Lead compounds PbCrO_4 , PbSO_4 , and PbO are used to produce yellow and green dyes and pigments [39]. Lead is also part of white ink. The main component of cyan in the colour printing processes is copper (II) phthalocyanine blue ($\text{C}_{32}\text{H}_{16}\text{CuN}_8$). Nickel occurs as part of multiple colourants [40].

The content of major elements and selected trace elements in CB is shown in Table 4. The source of the major inorganic elements in the waste paper is the filler used. By concentration, major elements form the series $\text{Ca} > \text{Si} > \text{Al} > \text{Fe} = \text{K} = \text{S} > \text{Ti}$, while the order of trace elements is $\text{Mn} \gg \text{Zn} > \text{Cu} > \text{Pb} > \text{Ni} = \text{Cr}$.

Table 4. Chemical composition of inorganic elements in waste paper and paper briquettes.

Waste Paper	Al	Si	Ca	Fe	Ti	P	S	K	Cl	Mn	Cr	Ni	Cu	Zn	Pb	As
	%															
	mg/kg															
PB	0.67	1.76	7.85	0.23	0.11	0.12	0.21	0.22	263.6	520	7	9	54	95	25	3
WOP *	0.036		8.50	0.37						260			14			
Card board **	0.034–1.14										0.5–6.2	0.9–4.9	0.2–16.7	1.4–61.3	1.4–12.8	
Paper ***	0.03–1.14										0.5–2.7	1.03–3.3	0.5–17.3	3.0–10.1	1.4–12.8	
Paperboard ***	0.14–0.56										0.9–2.7	0.9–2.5	0.9–49.7	1.4–7.4	1.5–11.1	
Corrugated board ***	0.12–0.40										1.3–6.2	2.5–4.9	0.2–166.6	14.0–61.3	1.4–12.8	

Explanations: * Wang et al. [41]; ** Mertoglu-Elmas [42]; *** Elmas and Çınar [37]; WOP—Waste office paper.

The high Ca content is related to the use of calcium carbonate or calcium sulfate as a filler (0–25%) in the production of paper [41]. Silicates may also be used as a filler—clay, talk and oxides (titanium oxide). Mn is a biogenic element derived from wood biomass that occurs in wood and wood biomass at a concentration of 430 mg/kg [43]. As a filler and for enhancement of coating, Zn is used in the form of ZnO , ZnS , and lithophone (a blend of BaSO_4 with ZnS) in the production of cardboard products [42], which explains the highest levels of Zn in PB compared to WM and CB. Manganese is present in biomass as an essential element [44].

During repeated recycling of waste paper, there is a further increase in the concentration of Mn, but also of other elements Zn, Ni, Cu (Otto et al., 2021), which probably explains the higher levels than Elmas and Çınar [37] reported for the cardboard used in the food industry, where the content of selected trace elements is capped by the “Packaging Waste Directive 2018/852/EU” [45].

3.2.2. Waste Wood from the Furniture Production

The inorganic components contained in biomass and in biomass ash can be divided by their concentration into major (>1%), minor (1–0.1%), and trace (<0.1%) elements [46]. The bonding type of elements affects their release during the combustion process. Ash-forming elements (Al, Ca, Cl, Fe, K, Mg, P, Na, S, Mn, Si, and Ti) in biomass may be bound in an inorganic or organic component. The method of inorganic binding elements in biomass is described by Vassilev et al. [47]. Inorganic elements Al, Ca, Cl, Fe, K, Mg, Mn, Na, P, S, and Si associated with organic matter are bound directly in organic groups, complexes, matrix, and structures. Elements Ca, K, Mg, Mn, and Na are bound in carbohydrates, Fe in chelates, Cu, Mg, Mn, Mo, N, and Ti in chlorophyll, Ni in citrates, P and Si in esters. Phosphorus is bound by phospholipids, phytates [48] and in proteins where Mg, Mn, N, P, and S can also be bound. Ca and Mg are bound in pectates and oxalates together with K, Mn, and Na. Fe, N, and S may occur in binding to organic S (amino acids, sulfate esters, sulfolipids, sulfonates, and proteins. Organo-metallic compounds are formed with Hg and K [47].

In inorganic form, the biomass contains Ca, Mg, K, Na, Fe, and Mn, which are bound in carbonates, phosphates, and silicates, where Al and Ti also enter. Important inorganic phases are oxyhydroxides, which contain Ca, Mg, Fe, Mn, Al, and Ti. Elements Ca, Mg, K and Na. Ca, Na, K, and Al may be present in the form of sulfates. Moreover, in the original biomass, all inorganic elements also occur in a water-soluble form [43].

The most significant source of trace elements contained in virgin wood is the application of preservatives. Pesticides used for forest protection may contain Hg, Cu, Pb, Zn, Cd, Ni, Mn, and As in the form of calcium arsenate or sodium arsenate [40]. Chemical compounds used for surface treatment (siccatives) contain Zn, Cd, Pb, Cu, and Cr [49]. The most common wood-preservatives include chromated copper arsenate (CCA), Cu preservative without Cr (ammoniacal copper quaternary—ACQ, copper azole, copper citrate, and copper ethanolamine), boron and Al compounds [50,51]. Preservative-treated wood contains 1–2% of heavy metals [51]. Content of inorganic elements in WM, wood and wood treated with preservative collected from literature data are listed in Table 5.

Table 5. Content of inorganic elements in WM, wood and wood treated with preservative (literature data).

Wood Mixture	Al	Si	Ca	Fe	Ti	P	S	K	Cl	Mn	Cr	Ni	Cu	Zn	Pb	As
	(%)										mg/kg					
WM	0.32	0.81	1.51	0.22	0.02	0.77	0.03	0.21	68.4	300	4	7	20	200	8	2.4
Wood *	0.003	0.093	0.75	0.0005		BDL	0.015	0.02	114	100						
Bark *	0.009	0.02	0.83	0.0039		0.045	0.036	0.21	260	714						
STW **											60	3.5	59	440		53
STW ***—CCA											4300–9100		2800–5500			3100–7600

Explanation: * Werkelin et al. [52]; ** Krook et al. [49]; *** Kim et al. [51]; CCA—Chromated copper arsenate; STW—surface-treated wood.

The contents of major elements in WM decreases in the following order: Ca > Si > P > Al > Fe = K > S > Ti; and for trace elements Mn > Zn >> Cu > Pb = Ni > Cr. Zn is an essential element in plants [44]. In untreated stem wood (spruce) is a concentration of Zn < 100 mg/kg d.m. [53]. WM fuel contains a Zn concentration of 200 mg/kg, indicating the presence of Zn of anthropogenic origin (siccatives). The anthropogenic contamination of WM is also evidenced by the increased Al concentration, which is about ten times higher than the average Al concentration in plants—0.02 wt.% and the Fe/Mn ratio, which is >1 [54].

3.2.3. Elements in Coal

Elements in coal occur in different forms and concentrations depending on genetic conditions, most of the major elements being discrete minerals [55]. The presence of trace elements is linked to the degree of coalification [56]. Trace elements in coal may be present in many different forms; for example, they may occur in silicates, sulfides, carbonates, oxides, sulfates, phosphates, selenides, and halides, or they may be bound to the surfaces

of minerals or the organic matter. Gluskoter [57] already identified elements primarily bound to the inorganic component (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, and Zn) and elements bound to the organic component (B, Be, Ga, Ge, P, Sb, Se, and V). According to their organic or inorganic affinity, the different division of elements was developed by Lewińska-Preis et al. [58]. They distinguish the occurrence in mineral phases for Zn, Cd, Mn, and Pb, while the link to the organic component of coal (organometallic complexes, chelates or ion-exchange compounds) is typical for Co, Cr, and Cu. Organic compounds bound in lignite from the total content: 60% of Mg and Na, 50% of V, 35% of Al, Ca and Co, 30% of As and Ni, 25% of K, 20% of Cu, 15% of P, Ti and Zn, 10% of Cr and Mn, and 5% of Fe [56].

It is clear from Table 6 that the contents of the major elements correspond to the published concentrations. Only the measured concentration of Ca is significantly below the value reported under the certificate of Free Company and slightly below the value reported by Vassilev et al. [43]. A significant difference can also be seen in potassium. The measured concentration in CB corresponds to the data of Vassilev et al. [43], but it is about four times higher than the value reported by Free Company. Higher values in CB than those reported for coal lignite Clarke [59] were found for Mn and Cr, while other trace elements, including As, have lower values.

Table 6. Content of inorganic elements in CB and their comparison with literature values and coal Clarke values.

Coal Briquette	Al	Si	Ca	Mg	Fe	Ti	P	S	K	Cl	Mn	Cr	Ni	Cu	Zn	Pb	As
	%										mg/kg						
CB, REKORD 4	0.9	2.08	0.54		0.46	0.14	0.024	0.22	0.11	86	273	33	24	19	22	10	2.54
Free Company, s.r.o.	0.07	0.23	1.14	0.17	0.50			0.2	0.03								
Lignite *	0.71	3.04	0.79	0.20	0.56	0.07	0.0068	0.54	0.11	41.5	86						
Lignite **	0.74		1.86	0.11	0.67	0.03			0.04	120	72.7	13.3	32	19.5	28	ND	1.77
Coal clark lignite ***						0.072	0.02				100	15.0	9.0	15	18	6.6	7.6
Lignite ****	1.5		0.46	0.11	1.30	0.08	0.043		0.18		43	15.0	14	16	53	11	24

Explanations: * Vassilev et al. [43], ** Tomza and Kaleta [60], *** Ketris and Yudovich [59], **** Finkelman et al. [56].

The highest levels of major and trace elements Al, Si, Fe, Ti, Cr, and Ni were found in CB > PB > WM. The highest levels for Ca, K, Mn, Cu, and Pb were found in PB > WM > CB, while for P and Zn elements, the highest levels were found in WM > PB > CB.

3.3. Elements in Ash and Deposit

The behaviour of trace elements during combustion depends on their concentration, the form of occurrence, and how they are bonded to the organic or inorganic components of the coal and the combustion conditions [61]. Elements bonded in organic matter are vaporised and subsequently escape into the atmosphere or are adsorbed on small particles of ash during combustion in the boiler. Most elements that have a higher affinity for the inorganic matrix are usually non-volatile and tend to stay in the ash or fly ash [62].

Vassilev et al. [43] sorted the elements by the concentration of ash-forming elements in plant ash (141 biomass varieties) in the following order: O > Ca > K > Si > Mg > Al > Cl > P > Fe > Na > S > Mn > Ti. Elements Ca, Cl, K, Mg, Mn, Na, P, and S in ash from natural biomass normally show higher contents than the respective values for coal ashes, while Al, Fe, Si, and Ti show significantly lower values [43].

Based on the concentrations of major elements in ash from WM briquette combustion, the elements show a similar arrangement of Ca >> Si = K > Fe > Al > Mn > S > P > Ti as elements in ash from plant ash [43]. The series of trace elements in ash from WM burning is as follows, according to trace element concentration: Zn > Cl > Cu > Pb > Ni = Cr = As. Calcium levels in ash are up to five times higher than those of Si, a ratio that is maintained in deposits. The ash from WM has a significantly higher Fe content than plant ash [43]. Differences in Fe content are already evident in WM briquettes, which contain up to 15 times more Fe than wood biomass, according to Jensen et al. [63]. In addition,

Si has about nine times higher content in WM, and Al up to twenty times higher content than Jensen et al. [63] reported for wood. Increased Fe, Al, and Si concentrations may be related to the brushing of furniture wood. Garnet, aluminium oxide, silicon carbide and alumina-zirconia are used as abrasives.

When comparing the concentrations of elements in fuel (Table 7) and ash, the position of P has changed because it is highly volatile. The order of trace elements in ash has remained unchanged compared to the input fuel.

Table 7. Concentration of major and trace elements in ash and deposit (arithmetic mean and standard deviation).

Samples		Al	Si	Ca	Fe	Mn	Ti	P	S	K	Cr	Ni	Cu	Zn	As	Pb	Cl
		mg/kg															
		mg/kg															
		mg/kg															
AVG	BEC2	3.42	6.53	30.9	0.58	0.04	0.34	0.25	0.23	0.17	12.0	25.9	246	207	2.9	34.6	179
STD	PB-A	0.67	1.12	12.3	0.17	0.01	0.12	0.08	0.04	0.05	3.5	11.3	82.8	38.0	0.6	11.1	28.6
AVG	BEC3	2.33	6.29	32.8	0.48	0.17	0.36	0.34	0.28	0.34	30.0	24.5	221.9	171	6.2	56.9	462
STD	PB-A	0.46	1.34	14.1	0.14	0.08	0.17	0.06	0.07	0.11	7.6	8.3	75.1	41.8	1.4	17.4	157
AVG	BEC2	0.50	2.70	11.8	0.76	0.11	0.15	0.20	1.08	0.93	14.0	22.0	100.2	410	12.8	109	6000
STD	PB-D	0.21	0.39	3.13	0.24	0.01	0.02	0.02	0.21	0.21	3.2	8.0	21.9	98.6	3.3	29.9	897
AVG	BEC3	0.42	1.09	6.14	0.84	0.21	0.05	0.16	0.98	0.97	14.0	27.5	72.5	392	11.0	91.9	1460
STD	PB-D	0.12	0.33	1.44	0.31	0.02	0.015	0.02	0.17	0.29	2.6	5.2	10.6	87.5	2.9	18.7	350
AVG	BEC2	1.14	2.32	21.7	1.97	0.43	0.14	0.28	0.35	2.36	31.0	31.0	245	938	39.0	104	779
STD	WM-A	0.44	0.51	1.82	0.70	0.14	0.04	0.02	0.08	0.62	8.2	8.24	83.5	280	4.4	11.2	77.2
AVG	BEC3	1.24	3.11	12.8	2.17	0.34	0.19	0.28	0.33	2.67	48.0	57.0	221	2000	58.0	102	1217
STD	WM-A	0.19	0.40	1.21	0.44	0.12	0.05	0.03	0.14	0.56	15.0	12.0	64.4	457	8.0	7.8	115
AVG	BEC2	0.6	1.57	10.7	1.99	0.57	0.06	0.58	3.09	5.48	7.0	15.5	135	3000	43.0	202	2867
STD	WM-D	0.37	0.62	3.02	0.50	0.14	0.01	0.15	1.20	0.83	1.40	1.53	48.8	785	8.7	34.5	341
AVG	BEC3	0.57	1.33	5.41	1.96	0.25	0.18	0.28	1.71	3.73	24.0	12.0	149	6700	35.0	365.0	6989
STD	WM-D	0.07	0.14	0.50	0.36	0.02	0.03	0.02	0.30	0.18	8.3	4.56	32.0	921	7.3	86.3	759
AVG	BEC2	8.10	13.92	7.60	7.27	0.30	0.98	0.57	2.27	1.19	149	149	258	337	4.1	47.6	870
STD	CB-A	1.17	1.25	2.49	2.35	0.02	0.32	0.21	0.51	0.41	19.4	13.1	72.7	126	1.0	12.8	98.5
AVG	BEC3	7.16	13.07	6.78	8.36	0.15	0.90	0.49	2.72	1.23	174	158	302	409	4.8	45.5	750
STD	CB-A	0.48	0.36	1.04	1.40	0.03	0.12	0.05	0.38	0.18	17.7	13.3	107	99.4	0.6	15.9	87.5
AVG	BEC2	1.02	1.89	13.3	7.51	0.20	0.06	0.17	6.46	1.48	74.2	36.0	47.8	451	11.0	37.3	3026
STD	CB-D	0.28	0.42	3.22	1.95	0.05	0.02	0.06	1.29	0.72	16.5	11.3	12.4	116	2.3	12.8	824
AVG	BEC3	0.36	0.66	4.14	5.93	0.23	0.05	0.16	3.11	1.29	89.0	44.0	52.0	969	9.7	79.7	1389
STD	CB-D	0.06	0.12	0.75	0.70	0.03	0.04	0.02	0.32	0.16	18.4	12.3	6.42	22.0	2.5	8.7	428

3.4. Release of Elements into the Atmosphere during Combustion

The amounts of element release were quantified by a mass balance based on weight measurements and chemical analysis of the fuel and ash obtained, similarly to Sommer-sacher et al. [64]. The calculation was made on the basis of data on the total amount of fuel burned and the concentrations of elements in the fuel, the amounts of by-products of combustion, and the concentrations of elements captured in deposits and ash. The results, expressed as the percentage of the element released into the atmosphere from the burnt fuel, are highly relevant to the assessment of the environmental performance of domestic boilers (Figure 3). The amounts of elements captured in ash are shown in Table 8. Due to the small production and collection of particles in deposits (Table 2), the amounts of the captured elements are low. For PB and CB, the amounts of elements captured are <1% except for Cl and Zn (2.3%) for CB. In the case of WM, the production of deposits per kg/fuel was higher (8–10 g/kg), and the capture of elements is more significant, ranging between 10–15%.

Table 8. Amounts of elements contained in ash (%)—calculated from mass balance.

	<10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	>80
PB		K, S, Cl, Zn, As	Mn	Fe, P, Cr, Ni	Si, Ti	Al, Ca, Cu			
WM	P	Al, Si, Ni, Zn	Ti, S, Cr	Fe, K, Cl, Mn, Cu, Pb		Ca, As			
CB	As		Cr, Pb	Si, Ti, Ni	Al	K, Cl, Mn	S	Ca, P, Cu	Fe, Zn

The binding of elements in ash and their release into the atmosphere is primarily influenced by the form of the element in the fuel, which is probably more significant in terms of their release into the environment than the technological solution of domestic boilers.

Figure 3. Amounts of elements emitted during combustion from the stack expressed as a proportion of the total amount of elements contained in the burnt fuel (calculated from the values for both BEC2 and BEC3)—(a) paper briquettes PB, (b) briquettes from waste wood WM, (c) coal briquettes CB.

The most significant amounts of the major elements Al, Si, Ti, and P are released into the atmosphere from WM. The largest amounts of Ca, Fe, S, K, and Cl are released into the atmosphere from PB. Major elements are released in the lowest amounts from CB (Figure 3). Of the trace elements, the most significant amounts of Ni. The largest amounts of Cu and Zn are released from WM. The largest amounts of Mn and Pb are released from paper briquettes (PB). The largest amounts of As and Cr are released from CB. These results correspond to the mass balances from the joint evaluation of the two boilers, which were similar for both BEC2 and BEC3. Cases with a difference in the amounts of elements released into the atmosphere for the compared boilers > 20% are shown in Table 9.

Table 9. Relative differences in the amounts of the element released into the atmosphere resulting from a comparison between the combustion equipment.

PB		WM		CD	
BEC2 > BEC3	BEC3 > BEC2	BEC2 > BEC3	BEC3 > BEC2	BEC2 > BEC3	BEC3 > BEC2
	Al (45%), Mn (60%), Cr (70%)	Ca (25%), As (65%)	S (51%), Mn (32%)	Fe (56%), Cu (47%), Zn (36%)	Ca (38%)

The higher amount of Al released from the BEC3 boiler is probably related to the higher temperature that allows the decomposition of aluminium sulfate used in the production of surface treatment paper, which decomposes at 770–860 °C [65]. Manganese (Mn) in

biomass occurs as positive metal ions, which can be in the form of free ions or complexes. Metal ions may also be organically associated with biomass fibres [52] and can only be released into the air when they burn out.

The higher amount of Ca released from the BEC2 boiler during WM combustion is related to the degradation of calcium oxalate crystals [66] and the subsequent reaction of Ca ions with CO₂ to form calcite at >479 °C. Calcite decomposes at a temperature higher than 750 °C [67] for the creation of CaO. CaO has not been identified in ash and deposit products from BEC2 and BEC3 by the X-ray-diffraction method. The mineralogical analysis of ash shows that in the case of ash and deposits from BEC3, a greater amount of Ca is bound in an amorphous phase, which was formed at a higher temperature than was present in the BEC2 boiler. A surplus of Ca ions was released into the atmosphere. Wood preservatives containing As (arsenate) break down in the temperature range from 750–800 °C during de-arsenation [68]. The amount of sulfur in the BEC2 and BEC3 boiler emissions is affected by the thermal degradation of thioxanthene, which has been identified in the deposit products and in the input material by the Py-GC/MS method. Thioxanthene is a pyrolysis product formed by the thermal degradation of the thiophenol/formaldehyde resins [69] contained in WM. In addition to thioxanthene, other sulfur-containing organic compounds have been identified in the deposits from BEC2 from WM combustion—thiourea, tetramethyl thiourea, 3 methyl thiophene and dihydro 2,3H thiophenone, which are also produced during the thermal degradation of thiophenol/formaldehyde resins. For example, thiourea starts to isomerize to ammonium thiocyanate (NH₄SCN) at temperatures ranging from 140 to 180 °C [70]. The absence of these compounds in deposits from BEC3 explains the degradation of sulfur-containing organic compounds in the BEC3 boiler, and hence the higher sulfur emissions.

Results of the mineralogical analysis were also used to identify the differences between element release during the combustion of CB in BEC2 and BEC3. The results indicate that the amounts of maghemite in deposits from BEC2 (13.45%) and BEC3 (20.45%) vary significantly. In addition, hematite is also present in BEC3 (8.68%). Maghemite levels in ash from the combustion in both BEC2 and BEC3 are comparable (14.55 and 16.31%). Generally, higher amounts of Fe are bound in deposits from BEC3 in mineral Fe-phases than in BEC2. During combustion, iron distribution into individual phases—hematite, magnetite and Fe-glass phases—is affected by the O₂/CO₂ ratio [71]. With a higher O₂/CO₂ concentration, the proportion of magnetite increases and hematite decreases, while the amount of Fe-glass phase does not change. The amount of unburned carbon affects oxidation processes involving the formation of magnetite, maghemite, and hematite. After the complete burning of carbon, the magnetite present in the ash becomes completely oxidised to hematite [72]. Part of hematite and magnetite (approximately 8% of Fe) crystallises from the molten glass phases during combustion and is not significantly affected by changing combustion conditions [71]. Some trace elements are bonded to newly formed Fe-phases when coal is burned. For the deposits from BEC2 and BEC3, a polynomial dependence between Fe and Cu concentration was confirmed ($r = 0.84$, $n = 9$, $\alpha = 0.005$). Adsorption of heavy metals on the surface of iron oxides (mainly magnetite) in preferential order of Pb, Zn, Cu, Cr, and Cd or their substitution in minerals with spinel structure is known [73]. In the case of Zn, correlation between Zn and Ca has been demonstrated ($r = 0.81$, $n = 9$, $\alpha = 0.01$).

Differences in the behaviour of both major and trace elements during the combustion in BEC2 and BEC3 are primarily due to the presence of elements in the input fuel and the decomposition ability of phases in which both major and trace elements are bound and influenced by temperature and oxidation-reduction conditions.

In recalculation on the element content of the input fuel, up to twice as many major elements (55 g/kg) were released from PB during combustion compared to WM (28 g/kg fuel for BEC2 and 19 g/kg for BEC3) and CB (BEC2 21 g/kg and BEC3 23 g/kg). Calcium (up to 37 g/kg of fuel) accounts for the major proportion of elements released when PB is burned (Figure 4). The concentration of emitted elements when burning PB decreases

in the following order: $\text{Si} > \text{Al} > \text{Ca} > \text{Ti} > \text{S} > \text{K} = \text{Fe} > \text{P}$, and for trace elements: $\text{Mn} > \text{Cl} > \text{Zn} > \text{Cu} > \text{Pb} > \text{Ni} = \text{Cr} = \text{As}$. The high sulphur emissions from burning PB are due to the presence of organically bound sulfur, which is part of lignin sulfonate, a by-product of the sulfite pulping process [74] used to glue cartons [75]. The thermal stability of sulfonic groups is rather weak, as indicated by the low-temperature evolution of SO_2 . The decomposition is done in two stages at a temperature of between 120 and 360 °C, and the lignin component [76] decomposes from 360 to 700 °C. Cations (Na^+ and NH_4^+) bonded to the sulphonic groups strongly affect the decomposition of lignosulphonates. In the case of sodium sulfonate, sulphur is bound to Na_2SO_3 , or Na_2SO_4 and sulfides are formed under reduction conditions. The sulfonic group with NH_4^+ releases NH_3 at 270 °C, breaking down the sulfonate group into SO_2 [76].

Figure 4. Major elements (Al, Si, Ti, Fe, Ca, S, K, and P) released from the burning of 1 kg of fuel in BEC2 and BEC3.

The comparison of individual fuels shows that when burning PB, 1 kg of fuel releases the highest amount of trace elements 630–830 mg/kg (Figure 5). The value is affected by a high concentration of Mn. Other monitored elements (As, Cu, Cr, Ni, Pb, and Zn) are emitted at a concentration of 121–128 mg/kg, which is lower than WM combustion emissions. In the case of printed cartons, the content of other elements of Sn and Sb is also increased in the flue gas [77]. The amounts of trace elements released when burning waste office paper and corrugated cardboard increases with temperature [78]. When burning waste paper at 750–950 °C, manganese (68–205 mg/kg of fuel) and lead (38–54 mg/kg of fuel) pass into flue gas [78]. In our case, the amount of Mn released into the air was about twice as high, with input paper briquettes containing Mn in concentrations up to 520 mg/kg. The combustion in the EC2 and EC3 boiler released Mn in amounts of 300 to 470 mg/kg of fuel and Pb in amounts of 18 to 20 mg/kg of fuel. Lead and zinc have a lower volatility of Zn during the combustion of waste paper at a lower rate of combustion. The behaviour of Cu is not affected by the rate of combustion [79]. When burning WM in BEC2 at the fuel ratios 2.5 kg/h and 4 kg fuel/h (BEC3), the differences in Cu, Pb, and Zn emitted were not significant.

When burning WM, the series of released elements is $\text{P} > \text{Si} > \text{Ca} > \text{Al} > \text{Fe} > \text{K} > \text{S} > \text{Ti}$, and for trace elements: $\text{Mn} > \text{Cl} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Ni} = \text{Cr} = \text{As}$. Phosphorus was released in the highest amounts; it can be completely released as gaseous phosphorus oxides during the combustion process when it is organically bound due to the high volatility of organic phosphorus compounds [80,81]. Potassium release into the air from burning waste wood was studied by Sommersacher et al. [64], who found lower amounts of K release for waste wood ($18.5 \pm 3.2\%$), hardwood chips ($32.8 \pm 12.0\%$), and softwood chips ($24.9 \pm 8.1\%$) than was demonstrated for the PB burning (54–56%). The contamination

caused by the presence of soil particles in biomass in the feedstock also affects potassium behaviour during the combustion process of compressed wood mass, where K is bound in silicate minerals, and thus the amount of produced K_2SO_4 is decreased, resulting in an increase in SO_x emissions [54].

Figure 5. Trace elements (As, Cr, Cu, Mn, Ni, Pb, and Zn) with chlorine released from the burning of 1 kg of fuel.

According to decreasing concentrations, the different concentration series of major elements released into the atmosphere was found during burning CB. Due to silicates contained in the coal briquettes, the order of elements is as follows: $Si > Al > Ca > Ti > S > K = Fe > P$, for trace elements $Mn > Cl > Cr > Ni > Cu = Zn = Pb = As$. The combustion of coal briquettes emits the lowest amounts of major elements (21–23 g/kg), and for trace elements 204–215 mg/kg (with Mn), and about 58 mg/kg without Mn. In terms of both major and trace element emissions, coal briquettes are a “cleaner” fuel than other fuels using waste products.

3.5. Relative Enrichment Factor Elements in Ash and Deposits

It is known from the literature that in the ash from coalburning, the concentration of trace elements increases with decreasing particle size, which is influenced by the specific surface and sorption processes [59,82]. Similar relationships are known for major elements (Ca, P, Mg, and Si) in ash from biomass combustion but for K, the opposite has been shown [43].

The highest amounts of fine-grained particles are present in samples of WM-D deposits, followed by PB-D (Figure 6). The comparison of the mean grain size (d_{050}) for WM-D (0.114 mm) and WM-A (0.265 mm) shows that the WM ash particles have a coarser character. PB combustion products show a similar trend. The mean particle size (d_{050}) for PB-D is 0.122 mm, and for PB-A, it is 0.249 mm. A completely different shape of particle size distribution curves was found for deposits from CB combustion (Figure 7), where BEC3 CB-D has a mean grain value of 0.71 mm (specked particles are present), while BEC2 CB-D has a mean grain size value of 0.42 mm. The shapes of the ash grain curves are almost identical; the mean particle size for BEC2 CB-A is 0.254 mm, and for BEC3 CB-A, it is 0.287 mm.

Figure 6. The grain size analysis of ash (A) and deposits (D), PB-A, PB-D and WM-A, WM-D.

Figure 7. The grain size analysis of combustion products from coal briquettes.

The average size of the particles that make up the deposits is significantly smaller than the ash particles except for BEC3 CB-D. Therefore, it can be assumed that there could be enrichment by both major and trace elements, even in this case. The relative enrichment factor (RE) defined by Meij [83] was used to monitor the acquisition of by-products of combustion. Meij [83] classified trace elements contained in coal on the basis of the relationship between the temperature and degree of volatilisation during the combustion in large energy sources (Table 10).

During the combustion of PB, higher values of RE were found for ash (except S, Mn, and Cl). When burning CB, major elements Al, Si, Ti, and Fe, and selected trace elements Cr, Ni and Cu have higher values of RE in ash, while cations Ca and K and trace elements Pb, Zn, and As have higher values of RE in deposits (Figure 8). Completely different results were obtained when burning WM. All monitored elements (both major and trace) have a higher relative enrichment factor RE in deposits (Figure 9). The highest values were found for Pb and Zn.

Table 10. Comparison of elements characterised by the RE value according to the classification of Meij [83].

	RE-BA	RE-FA	Meij [83]	D-CB	D-WM
Class I	ca. 1	cca1	non-volatile elements, equally distributed in bottom ash and fly ash	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th, Ti	Mn, P
Class II	<0.7				
IIc		$1.3 < \dots < 2$		K	Mn , As
IIb		$2 < \dots < 4$	volatile in boiler but condensation on ESP ash particles	S, Ca, Cl	S, Ca, K, Fe, Ti, Cu
IIa		>4		Zn , Fe	Zn , Pb , S
Class III	<<1		very volatile without condensation on ash particles	Cr, Ni, Cu, Pb, As	Al, P, Cr, Ni

Explanation: BA—Bottom ash; FA—Emissions of fly ash; **bold**—elements in accordance with the classification of Meij [83].

Figure 8. RE values for elements contained in ash and deposits from the combustion of CB (a) and PB (b); RE = Concentration of element in ash/ash percentage in the feed coal $\times$ Concentrations of elements in coal/100.

Figure 9. RE values for elements contained in ash and deposits from the combustion of WM.

Some regularities resulting from the behaviour of elements during the burning of coal [83] cannot be used to identify unauthorised fuels burned in domestic boilers for solid fuels, as documented by the results obtained from the burning of paper briquettes.

In the case of PB, all major elements and most trace elements (except Cu) have $RE < 0.7$, placing them among the volatile elements. In fuels where elements occur bound in the form of salts, they are released into the atmosphere during combustion, which reduces their concentration in the by-products of combustion, and they cannot be used to identify the fuel originally burned. However, identification of unauthorised fuels on the basis of the presence of organic compounds in deposits is possible [26].

The ratios of the mean concentration values of elements in ash and deposits are shown in Figure 10. Ratio values > 1 were found for Al, Si, Ca, Ti, Cr, Ni, Cu, and Fe, Mn (CB and WM only), and P (PB and CB only). The values of A/D concentration ratio > 1 confirm that the element is preferentially bound to ash. The other elements (S, K, Zn, Pb, Cl, and As) have a ratio value of < 1 for all fuels due to their preferred concentration in deposits. The results confirmed the higher volatility of trace elements Zn, Pb and As.

Figure 10. Ratios of concentrations of elements in ash/deposit (A/D) calculated from arithmetic mean values.

3.6. The Influence of Principles of the Circular Economy for Residential Heating Fuels

Primarily, the aim of the circular economy (CE) is to protect primary raw material resources, including wood. CE is a regenerative method in which raw material input, waste generation, emissions, and energy are minimized by promoting the circularity of material and energy achieved by repair, reuse, remanufacture, refurbishing, and recycling [84]. The use of wood residues for energy is a natural part of the circular economy of the forest and wood industry. The partial replacement of wood or wood by-products (sawdust, shavings) with wood-based waste paper and cardboard could make a significant contribution to saving primary raw materials, especially in areas where waste paper and cardboard cannot be reused for the paper industry. At the same time, this option reduces the proportion of waste dumped ineffectively in landfills.

With the addition of 50% cardboard to wood chips, the price of the fuel input drops by 50% [85]. A similar price drop in the use of cardboard for briquette production has not been confirmed in the Czech Republic, and in the production of mono-fuel from cardboard, the price is even higher than for wood briquettes or sawmill briquettes. The price of briquettes made from sawdust and kindling from the production of wood (WOOD briquettes) in the Czech Republic is EUR 2.20/10 kg, and the price of “MIXI” briquettes made with the addition of 20% pure cardboard paper is EUR 1.92/10 kg. The price difference is only 13% [86]. NIGHT briquettes are only made from waste cardboard, are the most expensive (EUR 2.71/10 kg), and have the worst thermal parameters. WOOD briquettes have the lowest ash content of $<1.47\%$ and the best higher heating value of 18.8 MJ/kg, MIXI briquettes contain $<6.5\%$ ash, and their higher heating value reaches 16.5 MJ/kg, and NIGHT briquettes have the highest ash content of 13.04% and a higher heating value of 15 MJ/kg. The use of “NIGHT” briquettes is specifically targeted at citizens who “want to be environmentally friendly”. The prices of briquettes on the market in the Czech Republic are highly variable. Novak & Novak Eko Co. (Česká Skalice, the Czech Republic) supplies

briquette “beech cubes” at a price of EUR 1.62/10 kg, and briquettes from deciduous trees at EUR 1.42/10 kg. Moreover, the price of briquettes changes significantly during the year. It is about 20% lower in the summer months. The price for 10 kg of EN-certified pellets plus A1 ranges from EUR 2.1–2.3/10 kg for one of the largest producers in the Czech Republic (BIOMAC Co.) and between EUR 1.8–2.0/10 kg for non-certified pellets [87]. The prices of pellets and briquettes are comparable. Their overproduction influences the price of both pellets and briquettes in the Czech Republic. In 2016, a total of 300,000 tonnes of pellets were produced, and 25,000 pellet boilers were put into operation. In 2020, forty factories in the Czech Republic produced 486,000 tonnes of pellets, and 40,000 pellet boilers were in operation. The greater part (67%) of their annual production goes to exports. Almost all (96%) of the pellets produced are EN plus A1-certified internationally [88]. Another important factor is the low price—the average price of wood pellets on the Ukrainian market is EUR 80–100, while the prices of this product in the European Union countries vary from EUR 180 to 220 for a tonne.

While there is an increasing pressure to use RES (Renewable Energy Sources) for residential combustion across Europe, the market price trends did not foresee any significant increase [89]. Prices fell between 2012 and 2016 from USD 208 to 190, and then rose slightly to USD 200 in 2018. A gradual increase in the cost of industrial wood pellets is expected to be likely, reaching above USD 250 per million tonnes by 2030.

The market situation was influenced by the global COVID-19 pandemic for almost all commodities, such as lumber, where prices have increased by up to 200% over the past three months. Compared to the situation before the pandemic, COVID-19 lumber prices are up a staggering 188% [90]. The price increase for lumber and wood products was also demonstrated by the Producer Price Index used in the USA, which rose to 400 (in 1982, the index value was set at 100), compared to 200 in 2015 [91].

However, many factors play a role in the choice of heating, and the price is one of several significant factors. Recently, the importance of circular economics principles has been increasing. The increasing demand for the use of chipboard panels for construction purposes will increase the pressure to recycle them, although this depends on the possibility of finding ways to detoxify them before recycling or utilization of natural resins as a replacement for synthetic resins [92]. These missing proportions of waste wood could be replaced by waste paper and cardboard. Currently, the technology and waste-reclaiming process that turns cellulose residue from cardboard into a fully recyclable construction material (Honext) are already available.

In terms of local approach, to ensure self-sufficiency in the biomass supply for residential combustion, and, based on experimental results on the amounts of elements emitted when burning paper briquettes, we recommend the production of briquettes with a maximum of 10% added cardboard. This will ensure compliance with the requirements for briquette quality according to “EN ISO 17225-3 Solid biofuels—Fuel specifications and classes—Part 3: Graded wood briquettes (3% ash for briquettes group B)”. It is also possible to combine it with the otherwise unused material with a minimal negative impact on the environment.

4. Conclusions

The basic parameter for assessing the environmental impact of domestic boilers is the amount of dust particles emitted. The amount of dust particles is related to the chemical nature of the particles (the presence of inorganic and organic components) and the form of the element presence and binding into the fuel matrix. A comparison between the combustion of fossil fuel (coal briquettes), biomass containing the minimum amount of waste wood (WM) which was prepared according to the requirements of the standard ISO 17225-7 [22], and briquettes from waste cardboard and paper shows that PB releases the highest amounts of major elements (up to 57 g/kg of fuel) into the atmosphere, while the corresponding values are 22–28 g/kg for WM and 22–23 g/kg of fuel for CB. Similar results were obtained for trace elements (As, Cu, Cr, Mn, Ni, Pb, and Zn) and chlorine.

Burning 1 kg of WM released 0.38–0.41 g/kg into the atmosphere. In the case of PB, it is 0.63–0.82 g/kg, and, in the case of CB, 0.20–0.21 g/kg. Major elements and quantities of unburned carbon decisively influence the overall production of emitted particles. A comparison of BEC2 and BEC3 boilers shows that the modification of the combustion conditions (the amount of air added) is involved in the change in the phase composition of the particles in the deposits from CB. In the case of optimal oxidation conditions, the combustion of CB produces hematite in addition to maghemite. When burning WM and PB in BEC2 and BEC3, differences in the amounts of elements released into the air were generally not significant. At the present time, the quality of combustion fuel has a significant impact in terms of reducing the amounts of elements released into the air. Any addition of waste materials (including wood) contributes to increasing the amounts of elements released into the atmosphere. It is very important to follow the rules of the circular economy, which emphasize further recovery of waste, but their further thermal recovery must respect information on the behaviour of elements during combustion processes.

Further research should include the verification of the possibility of producing “clean fuel” from cardboard by removing fillers and additives and an assessment of the economic and energy requirements of this production.

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Abbreviations

The following abbreviations are used in this manuscript:

A	Ash
BEC2	Boilers of emission class EC2
BEC3	Boilers of emission class EC3
CB	Coal briquettes
D	Deposits
EC	Elemental carbon
EC2,3	Emission class 2,3
EEA	European Environment Agency
EF	Emission factors
EMEP	European Monitoring and Evaluation Programme
F	Fuel
FC	Fuel consumption
MDF	Medium-density fibrewood
OC	Organic carbon

PB	Paper briquettes
PM	Particulate matter
RE	Relative enrichment factor
RWC	Residential wood combustion
STW	Surface-treated wood
TC	Time of combustion
WL	Water leachate
WM	Briquettes from waste wood and from the furniture production

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