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Assessment of pollution by potentially toxic elements of agri-food biomass combustion ashes under different temperature regimes

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Abstract: The article discusses the influence of temperature on the quality of ash produced from the combustion of biomass from the agri-food industry, as well as its content of potentially toxic elements (PTE) such e as Pb, Cd, As, Cr, Cu, Ni, Se, and Zn. Geochemical indicators, including E (Emission factor of metals into the atmosphere), Cf (Contamination factor for individual toxicity metals), PLI (Pollution load index), and DC (Degree contamination), were calculated in relation to the potentially adverse environmental impact of biomass fuels.

Introduction

Bio–waste and its utilization have been increasing enormously due to the generation and management practices aimed at creating a cleaner environment (Piechota et al. 2023). The rising energy demand, dwindling reserves of non-renewable fuels, and emissions from combustion have promoted the consideration of agri-food biomass as a viable energy source. Biomass, due to its availability and potential environmental benefits, plays a key role in the energy balance, particularly owing to its positive impacts on the natural environment and local economies. Various agricultural and forest-derived products, as well as residues from the timber industry, are suitable for highly efficient combustion in specially adapted boilers. Other biomass sources include straw, paper waste, cyanobacteria, industrial waste, detergents, household waste, aquatic plants and microalgae. So-called edible biomass sources include peanuts, sugar cane, soybeans, wheat, rapeseed and corn, while non-edible biomass sources include cooking oil, agricultural waste, industrial waste and microalgae (Gani et al., 2022).

In response to the energy crisis, there is s high demand for alternative – e.g. fuel sources to coal, particularly in individual households. The adoption of green technologies can significantly mitigate greenhouse gas emissions compared to conventional, non-environmental technologies (Hayford et al. 2023). Despite Poland's substantial reserves of hard coal, alternative heating methods have been increasingly adopted in recent years.

Biomass-fired boilers, in particular, have gained significant popularity among individual consumers. As large quantities of firewood are consumed in households, there is a growing need for a gradual transition from wood-based biomass to agricultural waste biomass.

However, the rational utilization of non-forest biomass requires a prior assessment of its fuel properties, including the determination of potential emissions of toxic elements into the atmosphere. Emissions are heavily dependent on the type of biomass burned, the combustion technology used, and boiler operation (EMEP/EEA 2019). Open biomass burning could pose a significant risk to human health by negatively impacting air quality (Mehmood et al., 2022).

It should be noted that the burning of biomass also causes the emission of pollutants into the environment (Uliasz-Bocheńczyk et al., 2021). Partial combustion co-combustion with coal and waste are sources of emissions, including particulate matter (PM), carbon monoxide (CO), nitrogen oxides (NOx) and volatile organic compounds (VOCs) such as polycyclic aromatic hydrocarbons (PAHs) (Klyta et al., 2023).

Pellets derived from plant-based waste are known for emitting the least amount of pollutants. In 2018, nearly half of domestic households in the country (45.4%) used solid fuel heating devices, primarily coal (GUS 2019).

The most common form of non-wood biomass used in households was processed wood (e.g., briquettes, pellets), accounting for 0.9%. Less commonly utilized were crops from energy plantations and straw, with agricultural waste fuels accounting for just 0.09% (GUS 2019). Global energy use from biomass sources is approximately 10-14%, reaching 90% in rural areas, while in urban areas, biomass energy is used in about 40% of cases (Gani et al., 2022).

The use of natural resources is closely aligned with both European Union and national legal regulations, which play a significant role in the supply of resources for renewable energy production (Molo 2016). It is estimated that biomass combustion worldwide may generate approximately 476 million tons of ash annually (Odzijewicz et al. 2022).

Worldwide production of walnuts in shells ranges from 2 million to 3.7 million tons per year, depending on various sources (Miladinović et al. 2020; Queirós et al. 2020). In Poland, walnut harvests amount to approximately 1,000 tons (GUS 2023). -

The demand for fruit and processed products continues to grow each year. During the production cycle, vast amounts of fruit waste are generated due to their inedibility and perishable nature, which significantly burdens the environment (Leong and Chang 2022). In Poland, apple pomace is primarily processed into cattle feed or used in spirit production. It is also used in the production of diet drinks, wines, fruit teas, ice cream, lozenges, snacks, dietary supplements, meat products, and instant products, as well as in confectionery production, where it increases the content of polyphenolic compounds and fiber. (Masiarz et al. 2019).

Pellets made from sunflower husks are often used in coal-fired power plants due to its high calorific value (21 MJ/kg), relatively low chlorine content, and resistance to biodegradation (Chiyanzu 2014; Kałużyński et al. 2018; Zajemska et al. 2017). In Poland, depending on the apple variety and the processing method employed, the mass of discarded apple pomace ranges from 20% to 25% of the processed raw material, amounting to 0.22 – 0.35 million tons. Cherry pellets, composed of compressed wood and cherry pits (industrial waste), were produced in Poland at a rate of approximately 166 thousand tons in 2021 (GUS 2023). Although cherry pits are not yet a widely used fuel; however, they may potentially become a heating resource in the future.

In Poland's National Plan for Energy and Climate for the years 2021-2030 (Ministry of Energy, Poland 2019), it is projected that the share of energy from renewable sources (OZE) in the power industry will reach 31.8%, with solid biomass contributing 11.5% of this total. So far, biomass combustion methods in Poland have mainly involved co-firing mixtures of forest biomass with coal in grate boilers and fluidized bed boilers, as well as co-firing dust mixtures in pulverized coal boilers.

The study aimed to assess the impact of agri-food biomass type and combustion temperature on the content of potentially toxic elements in the resulting ashes, specifically considering the potential use of biomass in individual home furnaces that lack flue gas dedusting devices. Commercial power plants co-burn biomass, mainly apple pomace and sunflower husks, with hard coal. However, the smallest ash particles can migrate through the chimney and enter the environment, while the stored ashes can affect soil and water quality. From an ecological perspective, it is crucial to understand the content of toxic metals in biomass ash to minimize their release into the environment. The accumulation of toxic metals in biomass ashes reflects their environmental concentration. Therefore, geochemical indicators such as Emission (E), Contamination factor for individual toxicity metals (Cf), Degree of Contamination (CD) and Pollution Load Index (PLI) were also calculated. Biomass (apple pomace, sunflower husks, walnut shells, and pellets from cherry pits and branches) was burned under laboratory conditions at temperatures of 400±15°C and 850±15°C. The basic biomass parameters (ash content, humidity, heat of combustion), granulometric composition, and the concentrations of potentially toxic elements (Cd, Cr, Cu, Ni, Cu, Pb, Zn, and Se) were determined. The research results are intended to help identify the most suitable biomass types for combustion at various temperatures without causing significant environmental risks.

Material and methods

Four types of agri-food industry biomass were analyzed: apple pomace (AP), cherry pellets (branches and pits) (CH), walnut shells (WS), and sunflower husks (SH). The biomass samples were desiccated at 100°C and subsequently pulverized using a cutting mill (SM 100) and an agate mortar. They were then ashed in a sylite furnace at temperatures of 400±15°C and 850±15°C.

The fundamental elements in the biomass samples were determined: carbon (C), hydrogen (H), nitrogen (N), total sulfur (S), chlorine (Cl), and oxygen (O). These analyses were conducted at the Measurement and Research Laboratories for Energy (ENERGOPOMIAR) in Gliwice. The content of C, H, and S was determined using an automatic IR analyzer (PN-EN ISO 16948:2015-07; PN-EN ISO 16994:2016-10). Nitrogen concentration was measured using the calorimetric method (PN-EN ISO 16948:2015-07), chlorine content through ion chromatography (PN-EN ISO 16994:2016-10), and oxygen content was calculated based on material balance (O = 100 – (C+H+N+Ash)). Ash content (PN-EN ISO 18122:2023-05) and total moisture content (PN-EN ISO 18134-2:2017-03) were determined using the gravimetric method. The calorific value of biomass was calculated computationally (PN-EN ISO 18125:2017-07).

The content of potentially toxic elements (PTE), including Pb, Cd, As, Cr, Cu, Ni, Se, and Zn, was determined using inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectrometry (ICP-MS/OES). These analyses were carried out in Canada by Bureau Veritas. The accuracy of analytical results was verified using standard certified reference materials.

The emission of PTE from biomass combustion was assessed based on emission factors for Pb, Cd, As, Cr, Cu, Ni, Se, and Zn released into the atmosphere in 2021, in accordance with data from the EMEP (European Environment Agency) report.

Particle size distribution analysis of the ashes was conducted using an Analysette 22 MicroTec analyzer, capable of measuring particle sizes ranging from 0.01 – 2000 µm, at the Faculty of Natural Sciences in Sosnowiec, Poland).

An attempt was made to evaluate toxic metal contamination in ashes derived from agro-food biomass using statistical methods applicable to environmental geochemistry. Calculations included emission factors (E), contamination factors for individual toxicity metals (Cf), Pollution Load Index (PLI) and the degree of contamination (CD) were calculated.

In this study, toxic metal emission factors (PTE) were calculated for 1 ton of burned biomass, considering its calorific value and the emission factors for the analyzed toxic metals reported in the European Environment Agency (EEA) report (2019). The general formula used to calculate emission levels, based on the emission factor per unit of chemical energy introduced into the fuel (KOBiZE – The National Centre for Emissions Management, 2023) is as follows (1):

$$E = B \cdot W_0 \cdot W \text{ [mg]} \tag{1}$$

Where:
E – emission of substances [mg], B – biomass consumption [Mg], W_0 – biomass calorific value [MJ/kg], W – emission factor [g/GJ] as defined in the KOBiZE report (2023).

Contamination indices (Cf) for metals in the biomass ash were calculated using the formula (2) (Tomlinson et al. 1980; Gope et al. 2017):

$$Cf = \frac{\text{C metal}}{\text{C background value}} \tag{2}$$

Where:
Cf - contamination factor for individual toxic metals
C metal – concentration of the metal in ash sample
C background value – background concentration of that metal

The Cf values are interpreted as follows:
Cf < 1 low contamination factor (low contamination); 1 ≤ Cf < 3 moderate contamination factor (moderate contamination); 3 ≤ Cf < 6 considerable contamination factor (high contamination); Cf ≥ 6 very high contamination factor.

The world average concentrations of Cu (45 μg/g), Ni (68 μg/g), Pb (20 μg/g), Cd (0.3 μg/g), As (13 μg/g), Cr (90 μg/g), Zn (90 μg/g), and Se (0.6 μg/g), as reported for shale by Turekian and Wedephol (1961), were used as the background values.

The Pollution Load Index (PLI) for biomass ash was calculated based on the Cf values using the following formula (3) (Gope et al. 2017):

$$PLI = \sqrt[n]{Cf1 \times Cf2 \times Cf3 \times \ldots \times Cfn} \tag{3}$$

It is defined as the *n*-th root of the product of the Cf values for individual metals (Kebonye et al. 2017).
where:
PLI - *Pollution Load Index*
Cf1, Cf2, ... Cfn – contamination factors for individual metals
The interpretation of PLI is as follows:
PLI = 0 indicates excellence,
PLI = 1 indicates baseline pollutant levels,
PLI >1 indicates pollution.

Håkanson (1980) introduced a research tool to simplify pollution control through the calculation of contamination degrees (CD). To determine the contamination degrees of biomass ashes in terms of potentially toxic elements (PTE), the sum of contamination factors (Cf) for toxic metals was calculated using the following formula (4):

$$CD = \sum_{i=1}^{i=n} Cf_{\text{Pb,Cd,As,Cr,Cu,Ni,Zn,Se}} \tag{4}$$

Where:
CD – contamination degree,
Cf - contamination factor for individual toxicity metals.
Håkanson (1980) proposed the following classification for contamination degrees (CD):
CD < 8 low degree of contamination,
8 ≤ CD < 16 moderate degree of contamination,
16 ≤ CD < 32 considerable degree of contamination,
CD ≥ 32 very high degree of contamination, indicating serious anthropogenic pollution.

Basic statistical tests were performed using Microsoft Office Excel 2016. The parameters determining measurement uncertainty included the arithmetic mean (n=7) and the standard deviation of the mean. Statistical parameters were calculated for all biomass samples from the agri-food industry. For PTE contents below the detection limit of the method, a value equal to half the detection limit of the respective analytical method was assumed for statistical calculations.

Results and discussion

Elemental analysis of biomass

The average values of essential biomass parameters obtained from the elemental analysis are presented in Table 1. The content of major elements in the ashes exhibits significant variation, with biomass CH containing the highest amount of ash (6.92%). Vamvuka et al. (2020) reported ash content in agri-food biomass to range from 1.4% to 7.3%.

The higher ash content in cherry pit and branch pellets (6.92%) (Table 1) is probably due to the mixture of these raw materials. Previous research on this type of biomass focused on cherry pit pellets or waste in the form of cherry twigs. This ash content of this biomass is higher than that reported in the studies by Rzeźnik et al. (2016) and Zając et. al. (2018).

The calorific value of fuel primarily depends on its moisture content and chemical composition, which mainly results from the diverse composition of organic substances extracted from biomass (Postrzednik 2014). The calorific values of the investigated biomass samples fall within a similar range (Table 1).

Table 1. Physical and chemical parameters of agri-food biomass and standard deviation (SD)

Sample / Parameter	**AP**	**CH**	**WS**	**SH**
Moisture content (%)	11.6 ± 0.21	9.4 ± 0.08	9.4 ± 0.13	10.8 ± 0.25
Ash (%)	1.87 ± 0.04	6.92 ± 0.21	0.76 ± 0.03	2.95 ± 0.13
Calorific value (MJ/kg)	16.06 ± 0.15	16.91 ± 0.29	16.86 ± 0.17	16.35 ± 0.34

AP - apple pomace; CH – cherry pellet; WS – walnut shells; SH – sunflower husks;
Data are presented average value ± standard deviation (n = 6, p = 95%)

Table 2. The average values of the elemental analysis parameters of agri-food biomass and standard deviation (SD)

Sample / Parameter (%)	AP	CH	WS	SH
C	49.10 ± 0.14	46.19 ± 0.17	50.43 ± 0.14	50.39 ± 0.15
H	6.54 ± 0.21	5.78 ± 0.18	5.99 ± 0.13	5.93 ± 0.16
N	1.44 ± 0.23	1.00 ± 0.23	0.40 ± 0.12	0.83 ± 0.03
S	0.10 ± 0.11	0.11 ± 0.11	0.01 ± 0.02	0.15 ± 0.15
Cl	0.026 ± 0.02	0.481 ± 0.28	0.042 ± 0.15	0.051 ± 0.11
O	42.79 ± 0.14	46.44 ± 0.16	43.13 ± 0.16	43.19 ± 0.14

AP – apple pomace; CH – cherry pellet; WS – walnut shells; SH – sunflower husks;
Data are presented average value ± standard deviation (n = 6, p = 95%)

The calorific value of walnut shells is lower than the values reported by Kazimierski et al. (2022) and Zajemska and Musiał (2013). In contrast, the calorific value of sunflower husks is similar to the results found in their studies. Rzeźnik et al. (2016) determined a higher calorific value for crushed cherry pits.

Moisture content in biomass can vary due to several factors, including harvest period, origin, transport, and storage. The moisture content in walnut shells and sunflower husks is slightly higher than that reported by other authors (Gazzali et al. 2013; Zajemska and Musiał 2013; Zając et al. 2018). The moisture content in cherry pellets is 9.4%, which is similar to the results of Jelonek et al. (2021) and Rzeźnik (2018).The average moisture content in apple pomace was 11.6%, which is higher than the value reported by Techera et al. (2024).

The comparatively low standard deviation (SD) values for the analyzed parameters indicate limited variability among the different biomass samples. Table 2 presents the mean values of the fundamental elements that constitute the biomass.

Chlorine, sulfur, and nitrogen are undesirable fuel components due to their harmful effects on the natural environment. Among the main elements, a higher nitrogen content was observed in biomass AP (1.44%) and chlorine content (0.81%) in biomass CH, compared to the other samples (Table 2). The nitrogen content in the tested biomass samples is consistent with the findings of several studies (Dołżyńska et al. 2019; Vamvuka et al. 2020; Islamova et al. 2021; Kazimierski et al. 2022). Biomass of agricultural origin often contains higher chlorine levels, which pose a risk of high-temperature corrosion to the steel structural components of boilers (Persson et al. 2007). The use of apple pomace biomass with higher nitrogen content in combustion may increase NOx emissions into the atmosphere.

Particle size distribution of biomass ashes

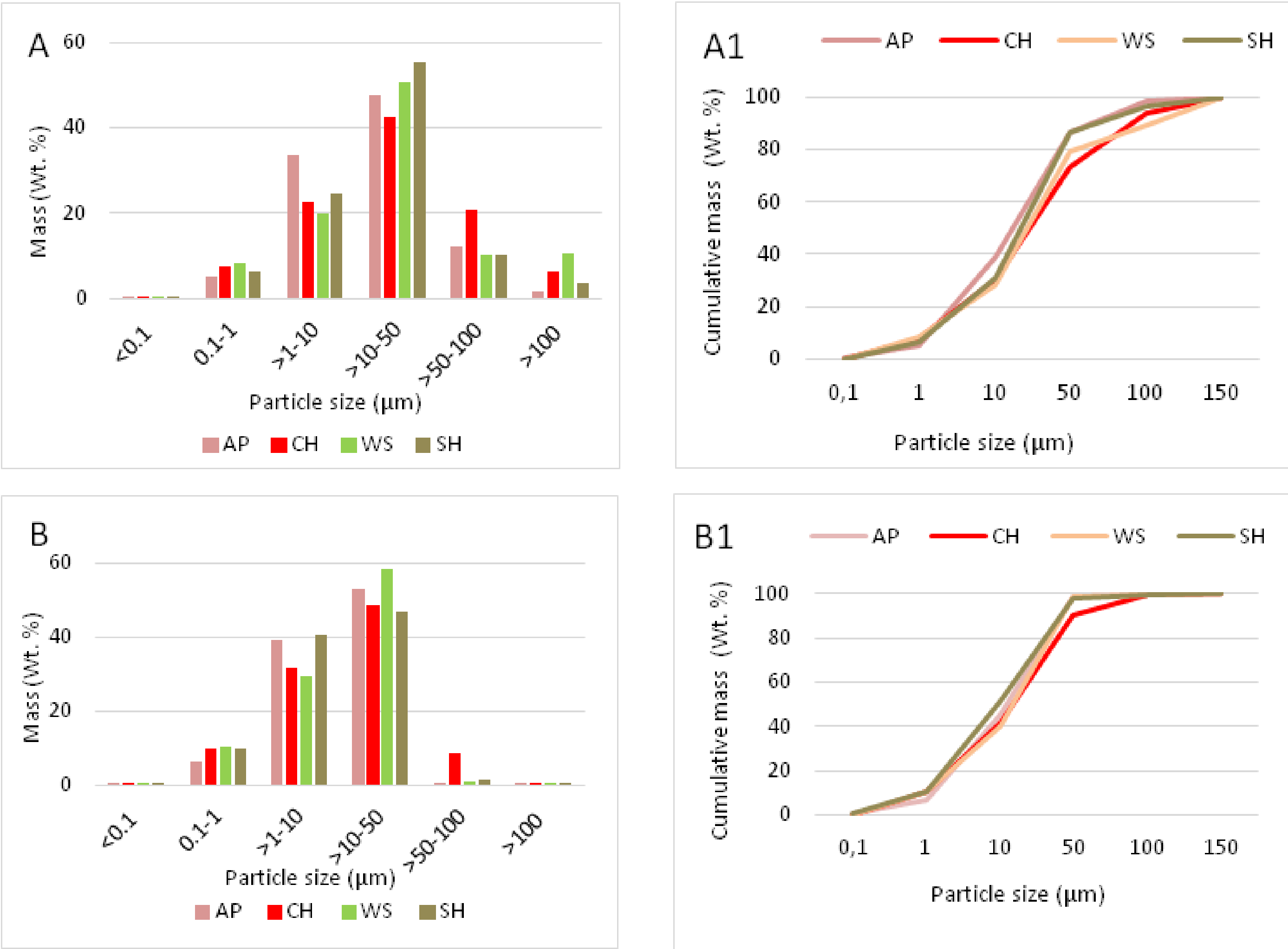
The granulometric analysis of the ash was carried out using the laser method with the ALYSEITE 22 from FRITSCH. This method is particularly effective for analyzing very fine particles, as the standard sieve method may introduce greater error. The particle size of the ash is crucial for atmosphere protection. Ashes from biomass combustion, regardless of biomass type and combustion temperature, typically exhibit a very fine particle size, with particle not exceeding 150 µm.

Figure 1 presents the results of the particle size distribution of biomass ash (Fig. 1 A-B) and cumulative particle size distribution curves (Fig. 1 A1-B1). The largest proportion of the total ash mass consists of particles in the size range of >1 – 50 µm. The percentage of particles within this range in biomass ashes produced at lower temperatures varies from 65.4% (CH) to 80% (AP) (Fig. 1A). In biomass ashes produced at a temperature of 850±15θ°C, the percentage of particles in the range of >1 – 50 µm is higher, ranging from 78.1% (WS) to 92.5% (AP) (Fig. 1B). The percentage of ash particles larger than 100 µm is slightly higher in ashes produced at a temperature of 400±15°C.

Based on the obtained results, it was found that the ashes formed at a combustion temperature of 850±15°C contain higher concentrations of the determined elements (except for Cd and Se). The very fine grain size of the ashes also contributes to a higher concentration of potentially toxic elements (PTE), which is expected given the small particle size.

Comparing the grain size of ashes from burned biomass is a big problem due to the diversity of presenting research results. However, various authors report that these ashes mainly consist of fine particles (Lanzerstorfer 2015; Cruz et al. 2017; Romero et al. 2017). According to Uliasz-Bocheńczyk et al. (2016), ashes from forest biomass and agricultural waste are primarily composed of particles smaller than 50 µm. The granulometric composition of ash from agri-food biomass further confirms the dominance of fine ash particles.

The results confirmed that laser granulometric analysis provides precise information on the size distribution of the finest particles. The accuracy of this method varies depending on the grain size range of the measured particles, with materials in narrower grain classes being analyzed most accurately.



AP – apple pomace (n=7); CH – cherry pellet (n=7); WS – walnut shells (n=7); SH – sunflower husks (n=7);

Figure 1 Granulometric composition of the produced ashes: A - particle size distribution and A1 - cumulative curve of the percentage of grain size (400±15°C); B - particle size distribution, B1 - cumulative curve of the percentage of grain size (850±15°C)

Content of toxic metals in raw biomass and ashes from its combustion

Figure 2 illustrates the concentration values of the analyzed PTE in raw biomass and the combustion products generated under different temperature conditions.

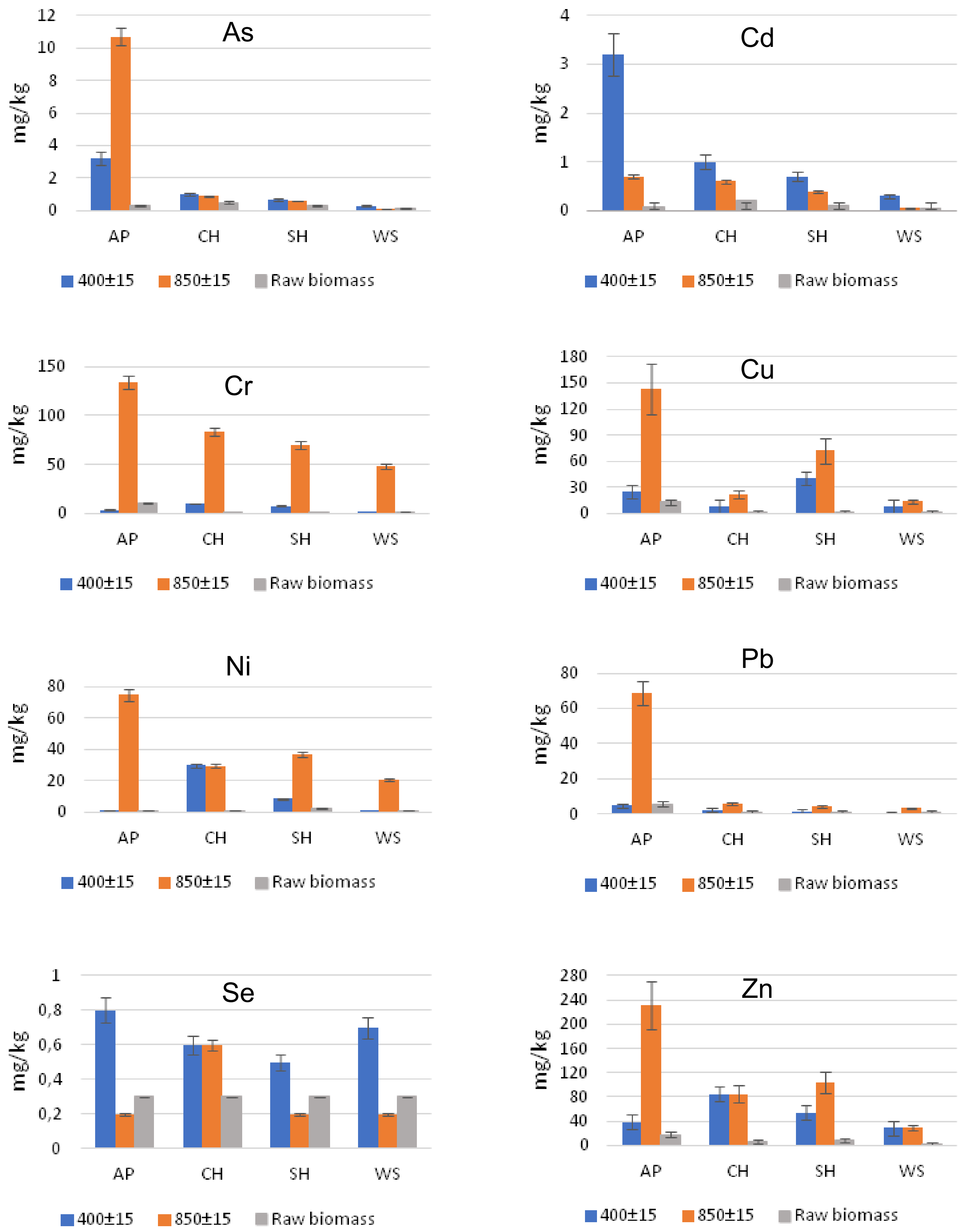
The analysis of PTE concentrations most often focuses on ashes from agri-food biomass. However, more data on the content of toxic metals in raw biomass is needed. Generally, these concentrations are low, as shown by the results for individual elements. Among the analyzed toxic metals, higher concentrations were found only in raw biomass from apple pomace (AP), with Zn (18.5 mg/kg), Cu (13.1 mg/kg), Cr (11.2 mg/kg), and Pb (5.8 mg/kg), being notably higher (Fig.2).

Ashes produced from biomass combustion exhibit greater diversity in toxic metal content. In all high-temperature biomass ashes, regardless of the biomass type, higher concentrations of As, Pb, Ni, Zn, Cu, and Cr were noted (Fig. 2). These elevated concentrations were particularly notable in ashes from AP biomass, with the content of Zn and Cu showing greater variability. In ashes generated from biomass combustion at 400±15°C, higher concentrations of Cd (3.8 mg/kg) and Se (0.8 mg/kg) were detected. Selenium values could not be compared due to the lack of data, while cadmium is typically determined only in whole fruits. The higher Cd concentration in ashes produced at 400±15°C from AP biomass increases as the temperature decreases, corroborating the findings of Odenberger et al. (1997).

In cherry pits pellet ashes, the average concentrations of Ni (29.8 mg/kg) and Zn (84.7 mg/kg) remained consistent regardless of the combustion temperature.

In sunflower husk biomass combusted at 850±15°C, the following concentrations were determined: Zn – 103.3 mg/kg, Cu – 72 mg/kg, Cr – 70 mg/kg, Ni – 36.7 mg/kg, and Pb – 7.01 mg/kg. Higher concentrations of Ni, Pb, Cr, and Cu were observed in the ash compared to the findings of Zając et al. (2019). However, when compared to the studies of Isemin et al. (2022), the concentrations of these toxic metals in the tested samples are lower.

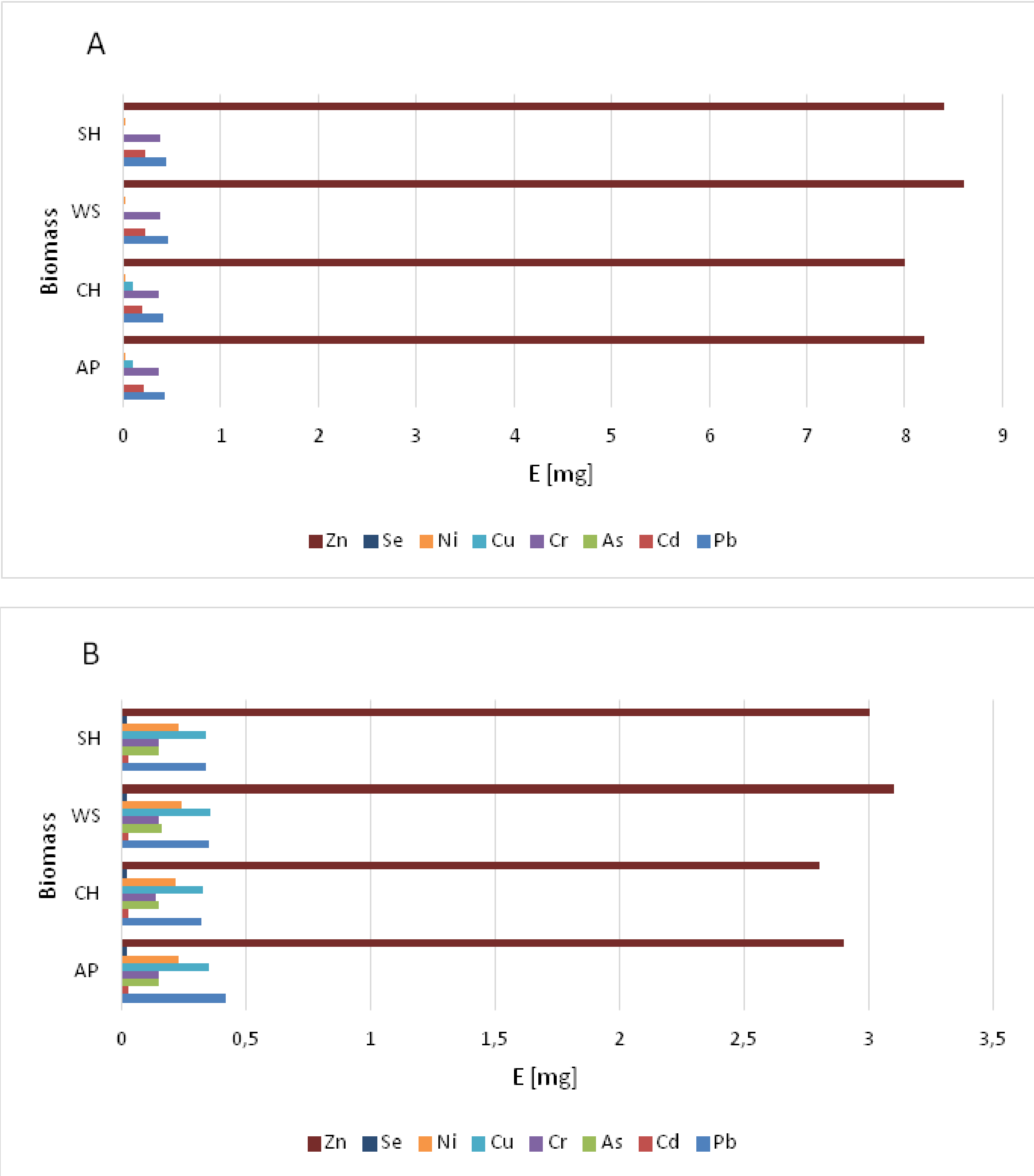
In high-temperature ashes from walnut shell biomass, higher concentrations were recorded for Cr (48 mg/kg), Zn (29 mg/kg), Ni (20.9 mg/kg), Cu (13.8 mg/kg), and Pb (3.2 mg/kg) (Fig. 2).These values are lower than those reported in other studies (Pastricakova 2004; Zając et al. 2019).



AP – apple pomace; CH – cherry pellet; WS – walnut shells; SH – sunflower husks;
As – arsenic; Cd – cadmium; Pb – lead; Ni – nickel; Zn – zinc; Cu – copper; Cr – chrome; Se – selenium;

Figure 2. Average values of PTE concentrations in raw biomass and ashes formed under various temperature conditions (400±15°C and 850±15°C). The results are the average value of seven samples for each biomass. The average values of PTE concentrations were supplemented with error bars with the mean's standard deviation value.

The diverse chemical composition of biomass ashes is influenced by the type of biomass and the conditions under which it is combusted (Vassilev et al. 2013). The accumulation of elements in biomass and their distribution within the plant depend on the species and stage of plant development. Moreover, environmental factors such as humidity and the availability of minerals in the soil significantly influence the accumulation process (Gworek et.al., 2003).



AP – apple pomace; CH – cherry pellet; WS – walnut shells; SH – sunflower husks;
As – arsenic; Cd – cadmium; Pb – lead; Ni – nickel; Zn – zinc; Cu – copper; Cr – chrome; Se – selenium:

Figure 3. Average emission values (E) from the combustion of agri-food biomass at temperatures of 400±15°C (A) and 850±15°C (B) were calculated based on seven measurement results for each sample

Table 3. Contamination factors (Cf), degree of contamination (CD), and pollution load indices (PLI) for ashes from biomass combustion at different temperatures

Sample (n = 7)	Cf								PLI	CD
	Pb	Cd	As	Cr	Cu	Ni	Zn	Se		
400±15°C										
AP	0.3	0.2	0.3	0.04	0.6	0.02	0.4	1.3	0	2.6
CH	0.2	0.4	0.1	0.1	0.2	0.4	0.9	1.0	0	2.4
WS	0.02	0	0	0	0.2	0.01	0.1	1.2	0	1.5
SH	0.1	1.0	0.1	0.1	0.9	0.1	0.6	0.8	0	3.7
850±15°C										
AP	3.4	2.2	0.8	1.5	3.2	1.1	2.6	0	12	14.8
CH	0.3	1.8	0.1	0.9	0.5	0.4	0.9	1.0	0	5.9
WS	0.2	0.2	0	0.5	0.3	0.3	0.3	0	0	1.5
SH	0.2	1.3	0.04	0.8	1.6	0.5	1.1	0	0	5.9

AP – apple pomace ; CH – cherry pellet; WS – walnut shells; SH – sunflower husks;
As – arsenic; Cd – cadmium; Pb – lead; Ni – nickel; Zn – zinc; Cu – copper; Cr – chrome; Se – selenium:

Assessment of biomass ash contamination

Emission levels depend on the type of fuel, fuel consumption, and the efficiency of the combustion equipment. The issue of harmful emissions from the combustion of raw and torrefied biomass primarily concerns wood and focuses on the measurement of CO, NO, CO_2, CH_4, and particulate matter (Böhler et al. 2019; Krumal et al. 2019; Maxwell et al. 2020).

Figure 3 shows the emission values (E) for the analyzed toxic metals, considering the temperature of biomass combustion. Ashes from agri-food biomass, irrespective of combustion temperature, exhibit higher zinc (Zn) emissions. Notably, Zn emissions are higher from ashes produced at lower combustion temperatures compared to those obtained from biomass burned at higher temperatures (Fig. 3B). Conversely, the calculated emissions of other toxic metals, such as Pb, As, Cu, and Ni, are higher for ashes generated from biomass burned at higher temperatures. For chromium, emissions remain consistent regardless of the biomass combustion temperature.

On average, approximately 6 tons of this resource are burned annually in biomass boilers used in individual household heating systems. The two most prevalent solid fuels are bituminous coal (36.5%) and firewood (28.8%), while other fuels, including various types of biomass (e.g., seeds, cereal grains, and energy plants), are less frequently used. Bituminous coal and firewood are often used concurrently or interchangeably in the same stoves. Among non-wood biomass options, formed wood products such as briquettes and pellets are the most commonly used in households, though they account for only 0.9% (GUS, 2019). The examined biomass raw materials, due to their low emission of toxic metals, present a viable alternative fuel source compared to wood, which is typically fired or co-fired with bituminous coal in individual household heating systems. However, zinc (Zn) emissions may pose a challenge, as they could exceed the levels indicated in this study. In Poland, many older, simple combustion stoves remain in use and are only gradually being replaced by modern installations with better combustion efficiency.

Emissions into the atmosphere strongly depend on the type of biomass burned, the combustion technology employed, and the operational efficiency of the boiler. Small-scale boilers often use grate combustion systems, which affect the emission levels of various elements, including zinc (Zn). The combustion of agri-food biomass in individual household heating systems remains primarily a theoretical possibility; in practice, such biomass types are rarely used or subjected to combustion processes. Additionally, ashes from these biomass types, like those from firewood combustion, are not typically registered or monitored.

Table 3 presents the contamination factor (Cf) values, pollution load index (PLI), and degree of contamination (CD) for the determined potentially toxic elements (PTEs) in ashes from biomass combustion under different temperature regimes.

The contamination factor (Cf) values for all PTEs in the ash samples from biomass combustion at the temperature of 400±15°C ranged from 0.02 to 1.3 and decreased in the following order:

AP: Se > Cu > Zn > Pb, As > Cd > Cr > Ni
CH: Se > Zn > Ni, Cd > Pb, Cu > As, Cr
WS: Se > Cu > Zn > Pb > Ni > Cd, As, Cr
SH: Cd > Cu > Se > Zn > Pb, As, Cr, Ni

In samples AP (Cf = 1.3) and WS (Cf = 1.2) combusted at 400±15°C, the highest Cf values were calculated for selenium (Se), indicating significant ash contamination with this element (Table 3). This is likely due to selenium forming complexes with toxic metals, including cadmium, which is present at higher concentrations in ashes produced at lower combustion temperatures (400±15°C) (Figure 2). The contamination factor for cadmium (Cf = 1) suggests a potential environmental impact, particularly with slight reduction in combustion temperature. It is evident that both the combustion temperature and the type of biomass are key factors influencing the presence of Se in ashes. Reducing conditions may also contribute to the concentration of Se by promoting the formation of compounds such as clausthalite (PbSe) and other selenides, including those of nickel (Ni) and copper (Cu) (Cappelletti et al. 2021).

The ashes from apple pomace (AP) produced at a temperature of 850±15°C are significantly enriched in Pb (Cf = 3.4), Cu (Cf = 3.2), Zn (Cf = 2.6), and Cd (Cf = 2.2), compared to other toxic metals (Table 3).

Cadmium in ash from cherry pellets (Cf = 1.8) and sunflower husks (Cf = 1.3) has a moderate environmental impact. The average values of the contamination factor (Cf) for ashes from biomass are presented in descending order of PTE values:

AP: Pb > Cu > Zn > Cd > Cr > Ni > As > Se
CH: Cd > Se > Zn, Cr > Cu > Ni > Pb > As
WS: Cr > Cu, Ni, Zn > Cd, Pb > As, Se
SH: Cu > Cd > Zn > Cr > Ni > Pb > As, Se

The highest pollution load index (PLI) values for potentially toxic elements (PTEs) were recorded in the AP sample (PLI = 12) at 850±15°C, indicating significant contamination of the ash with PTEs. For other biomass ash samples, PLI values were close to zero. Given these results, this type of biomass should be excluded as an alternative co-firing fuel with bituminous coal in industrial power plants. However, it may still be suitable for use individual household furnaces (e.g., briquettes or co-firing with coal and wood).

Considering the degree of contamination (CD) values for PTEs in biomass, the highest moderate value was determined in the AP sample (CD = 14.8) produced at a combustion temperature of 850±15°C (Table 3). For the other samples, regardless of the combustion temperature, the CD values were low.

The CD and PLI values in the AP ash sample can be attributed to the particle size of the ashes. Specifically, a higher proportion of particles in the range of 0.1 – 50 µm increases the surface area of the ashes, leading to a higher concentration of PTE on them. Such indicators are taken into account in studies of various environmental samples. Unfortunately, no literature would discuss these indicators in ashes from biomass combustion. However, ashes from the combustion of hard coal are taken into account, e.g. when using these ashes for recultivation or as an addition to the production of agricultural fertilizers.

Using geochemical criteria to assess the degree of ash contamination from agri-food biomass in PTEs allowed for an evaluation of their potential environmental impact. Most of the geochemical indices calculated for PTEs in biomass ashes formed at 400±15°C indicated low ecological risk. However, the contamination factor (Cf) and pollution load index (PLI) results showed moderate to significant toxic metal contamination in ashes formed at 850±15°C. This suggests that when co-burned with hard coal in the commercial power plants, this biomass could potentially contribute to increased pollutant levels in the ashes.

Due to the lack of available data in the literature, the calculated Cf, PLI, and CD indicators in biomass ashes cannot be directly compared. Therefore, further research is needed on ashes from agro-food biomass, with a focus on these geochemical indicators. This will provide insights into potential use of these ashes as a source of energy or for use in agriculture.

Conclusions

The findings of this investigation highlight the importance of both biomass type and combustion temperature as key factors influencing the variability in potentially toxic element (PTE) concentrations within ash residues. The analyzed raw biomass samples from the agri-food industry exhibited relatively low concentrations of PTEs compared to the ashes produced under different temperature conditions. Higher levels of elements such as As, Pb, Ni, Zn, Cu, and Cr were observed in the high-temperature ashes from apple pomace (AP), while elevated Cd and Se concentrations were observed in low-temperature biomass ash from AP. Additionally, PTE concentrations were higher in ash samples from cherry (CH), walnut shell (WS), and sunflower husk (SH) biomass ashes produced at 850±15°C. This can largely be attributed to the particle size distribution of the ashes, with particles within the size range of 0.1 – 50 µm constituting over 80% of the total mass.

The use of contamination factor (Cf), contamination degree (CD), and pollution load index (PLI) reveals that most ash samples were classified as having a low potential for PTE contamination. Exceptions include low-temperature AP and WS ash samples, in which Cf values for Se and Cd were moderately elevated. Moreover, the high-temperature AP ash sample exhibited a moderate CD value. The calculated atmospheric emission of Zn was relatively similar across the different biomass types, though it was slightly higher for ashes produced during low-temperature combustion processes.

The environmental risk associated with the combustion or co-combustion of agri-food industry biomass containing PTEs in the ashes must be effectively monitored. This is particularly important to ensure that its utilization, including storage, does not pose a threat to soils and water resources. As the research results demonstrate, only the combustion of apple pomace biomass may present a potential environmental hazard due to its higher concentration of PTEs. Providing detailed information on the origin of apple pomace biomass and conducting further research on PTE concentrations, particularly in different ash fractions, will be vital for its safe utilization.

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