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Biomass ash as a potential raw material for the production of mineral fertilisers

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Abstract. Ash obtained from biomass combustion could be a valuable product for fertilisation of soil or/and plant. It is connected with high reaction and potassium, calcium, magnesium content as well as low content of heavy metals. The analysed phyto-ash was obtained from Szczecin Power Plant Poland (12.2018–12.2019). The samples of phyto-ash, in the number of 24, were collected on subsequent dates at two-week intervals to determine the total content of the analysed elements (P, K, Mg, Ca, As, Cd, Ni, Cr, Pb, Hg). The differentiated percentage share of macro-elements both in total form as well as available form in ash from wood biomass and Agro-biomass is described as: calcium > potassium > magnesium > phosphorus. Phosphorus is characterised by a very low (10%) and highly variable availability. Ash from biomass is characterised by alkali pH (13.0). Biomass ash can be treated as a mineral fertiliser used for soil deacidification and as a substitute for calcium fertilisers. Biomass ash has a high content of potassium and magnesium, which could qualify this by-product as a source for fertiliser. Mean contents of heavy metals: lead, cadmium, arsenic and mercury in ash do not exceed the limit values for the mineral fertilisers. The variable percentage share of Agro-biomass did not result in significant changes in the amount of available form of macro-elements in ash. The obtained results indicate the pronounced variability, depending on the season in a year, of the content of available macro-elements in biomass ash.

Key words: biomass, macroelements, heavy metals, forest biomass ash, agro-biomass ash.

INTRODUCTION

THE DIRECTIVE 2009/28/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 April 2009 defines biomass as a biodegradable fraction of products, waste and biological residues from agriculture (including plant and animal products), forestry and related industries including fishery and aquaculture, as well as a biodegradable fraction of industrial and municipal waste (THE DIRECTIVE 2009/28/EC). The EU Directive does not prevent member states from adopting other definitions of biomass. In Poland, the Act of June 7, 2018 amending the Act on renewable energy sources and certain other Acts, defines biomass as a biodegradable share of products, waste or biological residues, biomass – solid or liquid substances of plant and animal origin, biodegradable, obtained from products, waste and residues of agricultural and forestry production and industry processing these products, as well as cereals grain which do not meet the qualitative requirements for intervention purchase (Journal of Laws of 2018, item 1276). Biomass of plant origin is produced through photosynthesis; $6CO_2 + 6H_2O + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2$. The most important chemical compounds are: cellulose, hemicellulose, lignin, pectin and waxes. The elements constituting biomass are mainly carbon, oxygen and hydrogen. In the process of oxidation, more specifically combustion, solid carbon is the main source of energy. The additional energy for the oxidation process is provided by hydrogen, and oxygen sustains oxidation. Utilization of biomass for energy is based on the idea that it is a carbon neutral fuel which will help cut greenhouse gas (Voshell et al., 2018). The chemical composition of biomass is greatly differentiated, to a great extent it is determined by the conditions of the biomass origin. Biomass is used for energy purposes mainly in the form of wood and waste from wood processing, energy crops, agricultural products, organic and municipal waste as well as sewage sludge. As an energy source, biomass can encompass waste from wood processing and cultivation (e.g. bark, sawdust, straw) or intentionally obtained product energy crops (Mierzwa-Hersztek et al., 2019). Burning biomass is conducive not only to obtaining energy, but also to improving environmental protection, (Żelazny & Jarosiński, 2019).

A distinction is made between forest biomass (wood biomass) and non-forest (Agro-biomass). The forest biomass includes wood not meeting standard quality requirements, forestry waste and residue, wood industry waste and residue excluding standard quality wood. The non-forest biomass includes solid and liquid substances of plant or animal origin, waste and residue from agricultural production and industry processing these products, the remaining waste, biodegradable parts, cereals grain not meeting standard quality requirements and energy crops. The most common in Poland are: basket willow, (*Salix viminalis*), sharp-leaf willow (*Salix acutifolia*), poplar (*Populus*), Jerusalem artichoke, (*Helianthus tuberosus* L.), the giant miscanthus (*Miscanthus* x *giganteus*) and multiflora rose (*Rosa multiflora* Thunb.).

The simplest technique of thermal processing is biomass combustion. However, the use of such a heterogeneous fuel results in producing ash which is an environmental challenge. Biomass combustion is universally recognised as being more ecologically friendly than fossil-fuel combustion, owing to a significantly reduced carbon dioxide emission. The basic solid fuel in the form of biomass is forest biomass, however agricultural biomass and the resulting fuels are gaining importance. It is evident that the composition of ash is determined by the type of biomass that is combusted. In comparison to coal, biomass is characterised by a markedly higher content of calcium oxide, potassium and phosphorus as well as variable, yet high at times, content of chlorine. In their analysis of the chemical composition of phyto-ash samples, Diatta & Kowalski (2017) demonstrated that the basic constituent was calcium oxide, with the exception of ash from wheat straw and rapeseed straw where silica was predominant.

Zając et al. (2018) combusted 35 types of biomass (trees and energy crops) and found that the dominant macro-elements in the chemical composition of ash were calcium, potassium, phosphorus and sulphur, which points to the possibility of using ash in agriculture. However, the use of ash from all types of biomass regarding its chemical composition is to be determined on an individual basis depending on the origin of given biomass. The authors provide the qualitative assessment of the share of particular macro-elements in ash depending on the combusted plants and found that the most abundant elements is ash from combustion of hardwood are: calcium > potassium > phosphorus, whereas in ash from combustion of conifers: calcium > silicon > potassium. The most abundant elements in ash from straw are: potassium > calcium > chlorine > phosphorus, and in ash from grass straw: calcium > potassium > calcium > chlorine. In the analysis of ash composition, the following elements are recognised: Si, Al, Ca, K, Na, Mg, Fe, P, Ti, The chemical composition of the mineral matter of ash varied between the samples, however CaO, SiO_2, K_2O, MgO, P_2O_5 and Al_2O_3 are the main compounds of ash (Magdziarz et al., 2018).

In ash from biomass combustion, 229 minerals and phases were identified. Predominantly they are: silicates, oxides and hydroxides, sulphates, phosphates, carbonates, chlorides, nitrates, silica, calcite, anhydrite, periclase and hematite (Vassilev et al., 2013). The content of alkali (sodium, potassium) in biomass is generally high, similarly to the content of chlorine and sulphur (Kassman, 2012). Alkali metals are found in ash predominantly in the form of sulphates, carbonates and chlorides. At high temperature, the decomposition of carbonates, sulphates and silicates is possible, for example in the reaction of $CaCO_3$ (s) → CaO (s) + CO_2 (g) (Johansen et al., 2011). However, Shao et al. (2012) found that the main components of ash from wood biomass combusted at sufficiently low temperature are: potassium carbonate, magnesium carbonate, sodium carbonate and phosphates.

In the composition of biomass, the presence of sulphur, nitrogen and chlorine is not to be overlooked as it may affect the level of harmful emissions due to combustion. The biomass produced from straw shows a high content of chlorine and relatively low content of sulphur. The important concern is the active corrosion in the process of combustion of biomass rich in potassium, chlorine and sulphur. During straw combustion, potassium can react with chlorine and be released in the form of KCl (Boström et al., 2011). At higher temperature, predominant is the sublimation of KCl, formation of which is determined by the amounts of chlorine.

Vassilev et al. (2013) indicate the disadvantages related to the composition and properties of biomass, such as: the presence of alkaline and halogen elements as well some dangerous trace elements, highly variable composition including moisture content (10–60%) determined by the type of biomass and seasoning period. The main environmental, economic and social benefits compensate for technological barriers and other issues resulting from disadvantageous composition and properties of biomass.

The Regulation of the Minister of the Environment of January 20, 2015 on the R10 recovery process classifies ashes from biomass combustion (i.e. phyto-ashes) and codes them as 10 01 03 (fly ash from peat, untreated wood) classifying it as mineral waste, as well as identifying the conditions of them being used as a fertilising material. One of the conditions is the requirement of meeting the limit values for fertilisers (Journal of Laws of 2015, item 132). Phyto-ash is the source of nutrients (Ca, K, P, Mg, Zn, Cu, Fe, Mn) for plants, has deacidifying properties and can be an alternative to mineral fertilisers.

However, the presence of harmful substances, particularly heavy metals, can be problematic. Ash from biomass can also contain trace elements, e.g. arsenic, cadmium, chromium, copper, mercury, lead, nickel, zinc, barium, molybdenum, vanadium, manganese, cobalt and antimony. Trace elements in ash are predominantly heavy metals. Heavy metals, among others Mn, B, Ba, Cu, Sr, Ni, Cr, Zn, Cd, Co, constitute merely 0.1÷0.3% of ash mass, however mercury is found in trace amounts and is usually within the range of 0.01÷1 ppm (Warren & Dudas, 1988).

The chemical composition of ash originating from biomass combustion is varied and determined by a number of factors, such as: the type of biomass, the species or specific parts of the plant, growing conditions, the age of plants, applied fertilisation, dosage of plant protection products and the date of harvest. The said factors can results in an increase or a decrease of element contents in biomass ash. Therefore, owing to the high variability of the quality of ash resulting from the type of the combusted biomass, a detailed analysis of its chemical composition is required prior to determination of the means of its utilisation, particularly as fertiliser (Zając et al., 2018).

Soil fertilisation is applied to maintain the appropriate level of soil parameters and produce high quality yield, therefore the chemical composition of phyto-ash is to be explicitly determined both quantitatively as well as qualitatively (Stankowski et al., 2018).

In summary, due to its chemical composition and alkaline reaction, biomass ashes can be tested for suitability as a mineral fertiliser. Due to the diversity of their origin, a careful analysis of their chemical composition, depending on many factors, is justified.

The aim of the present paper was to analyse the chemical composition of phyto-ash depending on the date of combustion (22.12.2018 – 13.12.2019) and the percentage share of wood biomass or Agro-biomass as well as the assessment of phyto-ash in terms of its usefulness in the production of mineral fertilisers.

MATERIALS AND METHODS

Experiment characteristics

The analysed phyto-ash was obtained from Szczecin Power Plant, Poland. Biomass was combusted in a bubbling fluidised bed (BFB) boiler by the Finnish Metso (https://pl.wikipedia.org/wiki/Elektrownia_Szczecin). The samples of phyto-ash, in the number of 24, were collected on subsequent dates at two-week intervals from 22.12.2018 to 13.12.2019, with a month's interval in the boiler's operation in June 2019.

Chemical analyses

On each subsequent date, a sample of 5 kg of ash was collected. Following the mixing, two samples of approx. 0.5 kg were collected from each sample, and the analytical samples of 250 mg were weighed for the analysis. To determine the total content of the analysed elements (P, K, Mg, Ca, As, Cd, Ni, Cr, Pb) in ash, the samples were mineralised in a sealed microwave system (Anton Paar Multivave 3000). A two-step procedure was employed using a mixture of concentrated nitric(V) and hydrofluoric acids (step one) and the addition of 4% boric acid to eliminate the excess F^- (step two). As the reference material, Polish Certified Reference Material Fine Fly Ash (CTA-FFA-1) was used.

Total content of As, Pb, Cr, Ni and Cd was identified with the method of inductively coupled plasma mass spectrometry (ICPMS); K, Mg, Ca was identified with ion chromatography (IC); P content was determined spectrophotometrically.

Determining the total content of mercury, ash samples were wet mineralised in the mixture of concentrated nitric(V) acid chloric(VII) acids using the Bethe set in CV-AAS method, the pH of ash (pH_{KCl}) was determined potentiometrically with KCl solution of 1M concentration in accordance with (ISO standard 10390 2005).

The available forms of phosphorus and potassium in soil were determined using the Egner-Riehm method based on the extraction of calcium lactate with buffer solution characterised by a pH value of 3.55 (Egner et al., 1960).

The content of the forms of alkali metals (potassium, magnesium, calcium) potentially available for plants were identified following the extraction with 1M HCl at the soil to solution ratio of 1:10 Kabała & Karczewska, 2019). 1M extraction with HCl solution is commonly used in agricultural studies for the purpose of determining bioavailability of metals for plants. The content of metals in the obtained extracts was identified with IC method.

Reagents and materials

In the preparation of all solutions, 18 MΩ cm grade water from Milli-ORG Millipore Co. purification system was used. During the analysis, only the reagents of recognised analytical grade or suprapure were applied. Calibration standards were supplied by Perkin Elmer as stock standard solutions of 10 $\mu g\ mL^{-1}$. Working mixed standard solutions (2–200 $\mu g\ mL^{-1}$) were prepared by dilution stock standard solutions in 0.7% nitric acid. Daily check performance solution (Perkin Elmer) was used for the spectrometer optimization. The following Certified reference materials (CRMs) were used for validation the method: Soil 5 (IAEA) and Fine Fly Ash CTA-FFA-1 (INCT).

Instrumentation

To prepare samples and CRMs, analytical (Sartorius MC5) and micro-analytical (BP221S) balances calibrated using national mass standards traceable to the international standards were used. Philips PU 8625 UV/VIS spectrophotometer was employed for the measurement of absorbance of formed phosphomolybdate complex with the added molybdate followed by the reduction of the complex with hydrazine hydrate in aqueous sulphuric acid medium. Dionex 2000i/SP ion chromatograph was equipped with analytical column Dionex IonPac CS12A, conductivity detector CDM II and the suppression system ASRS 4 mm. The eluent used was 18 mmmmol$\cdot L^{-1}$ methanesulfonic acid, the flow rare flow 1 $mLmin^{-1}$. The ELAN DRC II inductively coupled plasma quadrupole mass spectrometer (PerkinElmer) with crossflow nebulizer with Scott double-pass spray chamber and Ni cones was used for multi elemental analysis. Instrument operation conditions are: RF power - 1,000 W; nebulizer gas flow rate - 0.92 $Lmin^{-1}$; Plasma gas flow rate - 15 $Lmin^{-1}$; auxiliary gas flow rate - 1.2 $Lmin^{-1}$; lens voltage - 6.25 V; detector mode - dual; measurement unit - cps; working mode - standard.

Statistical analysis

The obtained results were statistically developed by calculating the selected characteristics of samples. The data concerning the distribution per individual characteristics is presented in the form of histograms. To compare the means, the Kruskal-Wallis one-way non-parametric analysis of variance was used. The relationships between the variables were calculated using the Spearman rank-order correlation at the level $P > 0.05$

and 0.01 (Dunn & Clark, 1974; Hill & Lewicki, 2021). The calculations were made with the Statistical PL software.

RESULTS

Biomass composition

The main form of the fuel supplied to the boiler was forest biomass (on average 87.7%), Agro-biomass constituted approx. 12.3%. On particular dates of collecting the samples, the percentage share of Agro-biomass varied from 2.10% to 41.28%. Within the range of 0–5% there were 5 samples, 5–10% - 4 samples, 10–15% - 9 samples, 15–20% - 3 samples and over 20% - 3 samples (Table 1, Fig. 1).

Table 1. Characteristics of composition and percentage share of biomass types

No	Sample collection date	Amount of combusted biomass [Mg]				
		Forest	Agro			Sum
			Chips	Pellet	Chips and pellet	
1	22.12.2018	807	114.0	41.4	155.3	1,118
2	7.01.2019	905	119.6	19.4	139.0	1,183
3	21.01.2019	1,321	370.2	49.8	420.0	2,161
4	5.02.2019	1,810	0.0	84.8	84.8	1,980
5	19.02.2019	1,573	0.0	45.4	45.4	1,664
6	5.03.2019	1,331	0.0	81.3	81.3	1,494
7	19.03.2019	1,519	0.0	43.9	43.9	1,607
8	5.04.2019	1,158	125.4	42.6	168.0	1,494
9	19.04.2019	1,290	65.7	77.6	143.3	1,577
10	30.04.2019	1,353	3.0	78.8	81.8	1,517
11	16.05.2019	1,396	139.7	26.3	166.0	1,728
12	29.05.2019	1,370	129.1	0.0	129.1	1,628
13	1.07.2019	489	303.8	40.0	343.8	1,177
14	15.07.2019	1,019	115.8	46.8	162.6	1,344
15	01.08.2019	698	201.8	34.1	235.9	1,170
16	14.08.2019	770	166.9	15.9	182.8	1,136
17	30.08.2019	971	145.8	37.8	183.6	1,338
18	15.09.2019	733	0.0	20.5	20.5	774
19	30.09.2019	1,122	134.4	44.6	179.0	1,480
20	15.10.2019	1,173	135.2	46.3	181.5	1,536
21	30.10.2019	1,186	137.6	64.4	202.0	1,590
22	15.11.2019	1,536	193.7	58.3	252.0	2,040
23	30.11.2019	1,804	0.0	38.7	38.7	1,881
24	13.12.2019	896	0.0	21.9	21.9	940
Sum		28,230	2601.7	1,060.6	3662.2	35,555

The share of Agro-biomass in samples was entirely random, as is demonstrated by the value of rs Spearman's correlation coefficient close to zero. The share of pellets in total biomass was from 0.0 to 84.8 Mg and was by far lower than that determined in the mass of wooden chips. The amount of wooden chips varied from 0.0 to 370.2 Mg (Table 2).

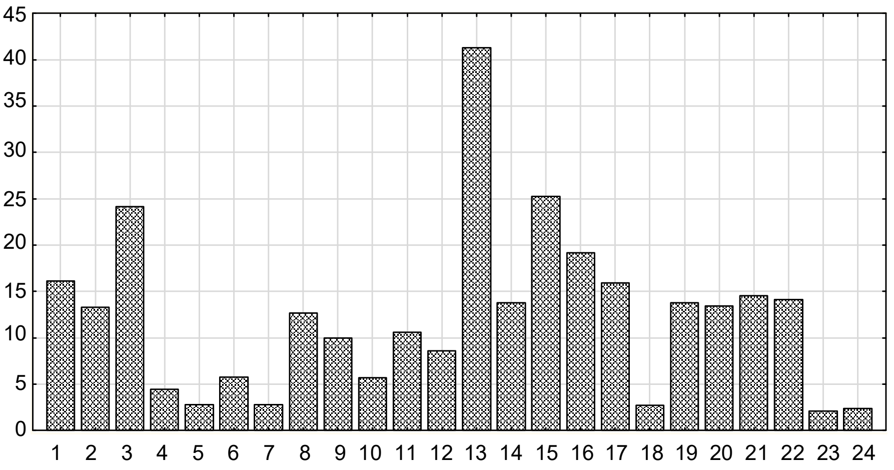

Figure 1. Share of agro biomass (%) in total amount of fuel: 1–24 – number of samples; 0–45 – % value.

Table 2. Statistical analyses of combusted material [Mg]

Type of biomass	Mean	Median	Minimum	Maximum	*V*%
Total amount of biomass fuel	1,481.2	1,371	774	2,161	25.0
Forest biomass	1,176.2	1,180	489	1,810	29.6
Wooden chips	108.4	122	0.0	370.2	91.6
Pellets	44.2	43	0.0	84.8	49.3
Wooden chips+pellets	152.6	159	20.5	420.0	63.7

V% – variability coefficient.

pH and macro-elements content

The analysis conducted on 24 samples of ash indicates that the most stabile feature of ash was pH (pH in KCl). Mean pH value amounted to 13.0, and variability was below 1% (Tables 3, 4). For comparison, the pH of the $CaCO_3$ aqueous solution is lower and amounts to 9 (Martín-Martínez 2002).

Table 3. Characteristics of macro-elements composition and pH of biomass ash (*n* = 24)

Trait	Unit	Mean	Median	Minimum	Maximum	*V*%
pH in KCl	%	13.0	12.9	12.7	13.2	0.82
Total calcium		13.76	14.2	5.33	18.05	22.16
Available calcium		11.9	12.3	4.27	16.90	28.47
Total potassium		5.55	5.37	4.02	7.39	15.05
Available potassium		4.43	4.69	1.65	7.35	32.55
Total magnesium		2.01	1.99	0.77	2.94	28.52
Available magnesium		1.58	1.51	0.49	2.56	34.77
Total phosphorus		1.43	1.36	0.748	2.32	29.8
Available phosphorus		0.136	0.090	0.004	0.401	88.4

V% – variability coefficient.

The ash in the experiment was characterised by a variable content of macro-elements. The largest amounts were identified for both total as well as available calcium; calcium from ash (Table 3). The distribution of data regarding available calcium supports the findings that it is asymmetrical and shows no consistency with the normal distribution (Fig. 2).

Mean potassium content in biomass ash was from 5.5 to 4.4%, respectively for the total and available form. The content of available potassium, showed greater variability than that of total phosphorus, - from 1.65 to 7.35%. The distribution of data regarding available potassium supports the findings that it is asymmetrical and shows no consistency with the normal distribution (Fig. 3).

The content of magnesium, another macro-element vital for plant growth, in ash ranged from2.0 to 2.9%, showed good availability for plants of 77% and relatively slightvariability of the results (*V*% respectively 28 and 35%) (Table 3).

The comparison of ash abundance in magnesium and potassium shows that the content of magnesium was by 50% lower than that of potassium. This relationship is to be taken into consideration when determining soil fertilisation dose.

Table 4. Correlation between time of sampling (x), pH and the content of soluble forms of macro elements in biomass ash

Dependent variability (y)	Spearman test rs value	Significance
pH	0.065	ns
Calcium	0.652	**
Potassium	0.681	**
Magnesium	0.723	**
Phosphorus	0.178	ns

ns – not significant correlation; ** – correlation at $p < 0.01$, very high significant correlation.

Figure 2. Distribution of results for plant-available calcium in ash from biomass.

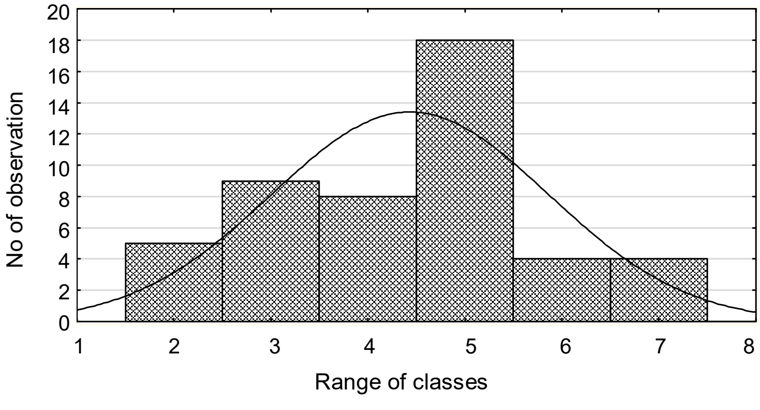

Figure 3. Distribution of results for plant-available potassium in ash from biomass ash.

Yet another issue is the content of phosphors in ash - phosphorus being, next to potassium and nitrogen, the most important constituent of fertilisers. The amount is relatively slight - the total phosphorus is, on average, 1.43% and the available phosphorus only 0.14%. However, the availability is merely at 10% thus it is very low and highly variable. The variability of the results for available form is at 88% (Table 3). The factor which greatly limits the availability of phosphorus is high pH of ash resulting in phosphorus presence in the form of sparingly soluble compounds. Most likely, bioavailability of phosphorus would increase following ash application to soil.

The results of the analyses of variance in which a different share of Agro-biomass was adopted as the factor, practically do not show differentiation of the content of available macro-components and pH in ash (Table 5). The results were found to be lower only for calcium and potassium with the lowest share of Agro-biomass (< 10%) in the combusted material.

Table 5. Effect of share of Agro-biomass (wooden chips + pellets) on chemical composition (available forms in %) of biomass ash

Share of Agro Biomass (%)	pH	Calcium	Potassium	Magnesium	Phosphorus
< 10	12.9^{a}	8.2^{b}	3.02^{b}	1.62^{a}	0.106^{a}
10–15	12.9^{a}	11.6^{a}	4.33^{a}	1.62^{a}	0.117^{a}
15–20	13.0^{a}	12.4^{a}	4.62^{a}	1.85^{a}	0.139
> 20	13.0^{a}	14.2^{a}	5.65^{a}	1.81^{a}	0.202^{a}

In order to obtain the results for individual seasons in a year, mean values were calculated (Table 6). The results show a significant differentiation of the content of available macro-elements in biomass ash. However, the aforementioned relationship does not apply to ash pH level, which is 13. In the winter season, the lowest percentage contents of available calcium, potassium and magnesium, i.e. metals, were identified in ash. As for the autumn season, the identified respective contents were found to be the highest.

Table 6. The effect of seasons in a year on the chemical composition (available forms in %) of biomass ash

Season	pH	Calcium	Potassium	Magnesium	Phosphorus
Winter	12.9^{a}	8.94^{c}	3.69^{b}	1.18^{c}	0.129^{b}
Spring	13.0^{a}	12.18^{b}	4.05^{b}	1.43^{b}	0.081^{c}
Summer	13.1^{a}	12.41^{b}	4.82^{a}	1.57^{b}	0.172^{a}
Autumn	12.9^{a}	14.38^{a}	5.31^{a}	2.09^{a}	0.163^{a}

a, b –mean values described by different letters, indicate significance difference.

Heavy metal content

The aforementioned Ordinance specifies the admissible limit values for pollutants in mineral fertilisers and substances enhancing plant cultivation (Journal of Laws No. 119, item 765 and 2009, item 1804). The values are to be considered when assessing the usability of biomass ash as a mineral fertiliser. Out of the six analysed heavy metals present in biomass ash, the limit values as specified in the Ordinance refer to only four: lead, cadmium, arsenic and mercury. Mean content in ash from wood biomass and Agro-biomass does not exceed the limit values specified in the current Ordinance (Table 7).

Table 7. The content of heavy metals and manganese in biomass ash and the limit content of heavy metals in mineral fertilisers according to Polish regulations

Trait	Units	Mean	Median	Minimum	Maximum	*V*%	Limit content in mineral fertilisers* [mg kg^{-1}]
Lead	mg kg^{-1}	73.3	75.0	25.2	122.6	25.73	140
Chromium		57.5	53.2	33.9	126.1	30.41	-
Nickel		30.9	31.3	15.1	48.2	20.68	-
Cadmium		16.8	15.8	4.2	29.9	45.17	50
Arsenic		7.7	7.2	1.9	14.6	38.14	50
Mercury		0.41	0.45	0.15	0.86	54.30	2

*according to the Ordinance of the Minister of Agriculture and Rural Development of June 18, 2008 on the implementation of same provisions of the Act on fertilisers and fertilisation (Journal of Laws No. 119, item 765 and 2009, item 1804); *V*% – variability coefficient

DISCUSSION

pH and macro-elements content

The deacidifying action of biomass ash results from high contents of potassium, calcium and magnesium compounds. In the process of combustion, in comparison to other elements, alkali metals compounds remain in ash and do not pass into the gaseous form. The problematic of the content of alkali metals in biomass ash is discussed in numerous scientific papers (Shao et al., 2012; Nunes et al., 2016; Kalembkiewicz et al., 2018; Magdziarz et al., 2018; Zając et al., 2018; Zhai et al., 2021). For comparison, Nurmesniemi et al. (2012), while burning biomass in a power plant, obtained a very similar value of ash pH 12.8. Żelazny & Jarosiński, (2019) obtained ash reaction from biomass, highly alkaline, pH in H_2O > 11. Therefore, significant losses of ammonia and phosphorus in the NPK fertiliser should be taken into account (decomposition of ammonia from the nitrate ammonia compound and the formation of phosphorus compounds insoluble in water in these conditions). Because of their properties and influence on soil chemistry, the utilization of wood ashes is particularly suited for the fertility management of tropical acid soils and forest soils (Demeyer et al., 2001).

The ash in the experiment was characterised by a variable content of macro-elements. Most of the inorganic elements assimilated by plants during growth remain in the ash after burning. They include plant macronutrients, for example, K, Ca, Mg, and P, which are the bulk of the materials accumulated in ash (Pasquali et al., 2018). Čepauskienė et al. (2018) differentiates the composition of ash depending on whether ash was obtained from wood biomass or agricultural residue. In the case of ash from wood biomass, the following chemical compounds were identified: $CaCO_3$, K_2SO_4, $K_2Mg(PO_3)_4$, $MnSO_4$. An analogous relationship is given by Jarosz-Krzemińska & Poluszyńska (2020). The total concentrations of macronutrients in the fly ash under study decreased in the descending order of nutritional elements Ca > K > Mg > S > P >. Through their experiment, they confirmed the predominance of calcium in ash found in numerous scientific papers, for example (Diatta & Kowalski, 2017; Magdziarz et al., 2018; Zając et al., 2018).

Similarly to the results of the analyses conducted in the course of the present study, most studies by other authors indicate that the amount of potassium in ash was secondary to calcium (Schiemenz & Eichler-Löbermann, 2010; Füzesi et al., 2015; Magdziarz et al., 2018; Zając et al., 2018; Zhai et al., 2021). Mean potassium content in biomass ash was from 5.5 to 4.4%, respectively for the total and available form. The content of available potassium showed greater variability than that of total phosphorus - from 1.65 to 7.35%. Generally, the amount of total phosphorus is five-fold higher than that identified in manure. For example, Schiemenz et al. (2011) report that the phosphorus concentration in biomass ash ranges from < 1 to 10%. Shi et al. (2017) present the conclusion that the introduction of all tested ashes increased the soil pH, the amount of exchangeable alkaline cations and available phosphorus, but decreased the exchange acidity of the soil. Kramar (2020) specified that about ¾ all the phosphorus contained in the ash is in a form accessible to plants, when interacting with soil, especially acidic. In the performed experiment, an analogous relationship was obtained (80%).

High abundance of total, as well as available potassium, indicates the realistic possibility of using ash for fertilisation purposes.

This could be explained by a lower content of calcium and potassium in stemwood in comparison to branches. According to Gornowicz & Pilarek (2013), the content of calcium in branches is from 0.13 to 0.29% and in wood tree-length from 0.09 to 0.22%, whereas with respect to potassium, the values for branches are from 0.05 to 0.15% and for wood of tree-length from 0.01 to 0.03%. Kramar (2020) reports that wood ash usually contains up to 15% K_2O in the form of K_2CO_3, 7% - P_2O_5 and about 40% CaO. The values for calcium and potassium are higher than those obtained in the performed experiment.

The results obtained in the experiment indicate a significant diversification of the digestible macronutrient content in the biomass ash. The aforementioned dependence is explained by the physiological processes of plants (trees). In spring and summer, trees take up large amounts of calcium, potassium and magnesium from the soil. Consequently, it may lead to the accumulation of elements in trees in the autumn period.

Heavy metal content

One of the factors determining the possibility of using ash for fertilising purposes is the presence of heavy metals. The toxic action of the said elements is connected with their ability to accumulate in the organisms of plants and animals.

When discussing the results of the present study, consideration should be given to a relatively high content of cadmium in ash - from 4.24 to 29.92, mean 16.81 mg Cd kg^{-1}. Other studies on cadmium content in ash from biomass of various origins show a lower content, for example 0.3 and 5.3 mg Cd kg^{-1} (Samaras, 2008). According to Poluszyńska & Ślężak (2015), the combustion of biomass from wood chips and sunflower husk pellets (79 and 21%) produced ash with 10.7 and 19.1 mg Cd kg^{-1}. The comparison of the composition of ash from wood and agricultural residue by Pastircakova (2004) demonstrates a higher content of As, Cd, Pb and Hg in wood ash.

The average and maximum content in ash from wood biomass and Agro-biomass did not exceed the limits set out in the applicable Regulation (Journal of Laws No. 119, item 765 and 2009, item 1804) which justifies the use of these ashes as mineral fertilisers.

CONCLUSIONS

Biomass ash is characterised by alkali pH. Mean pH value was 13.0 and its variability was below 1%. Biomass ash can be treated as a potential mineral fertiliser used for soil deacidification and as a substitute for calcium fertilisers. The ash from the experiment was characterised by a variable macro-element content which was subject to a very high random variability within a one-year long sampling period at two-week intervals. Biomass ash has a high content of potassium and magnesium, which could qualify this by-product as a source for fertiliser. Mean contents of four heavy metals: lead, cadmium, arsenic and mercury in ash from wood biomass and Agro-biomass do not exceed the limit values for the mineral fertilisers. The variable percentage share of Agro-biomass did not result in significant changes in the amount of available form of macro-elements in ash. The obtained results indicate the pronounced variability, depending on the season in a year, of the content of available macro-elements in biomass ash.

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