


## Article

# Repurposing Fly Ash Derived from Biomass Combustion in Fluidized Bed Boilers in Large Energy Power Plants as a Mineral Soil Amendment

Elżbieta Jarosz-Krzemińska <sup>1,\*</sup>  and Joanna Poluszyńska <sup>2</sup>

<sup>1</sup> Department of Environmental Protection, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Al. A. Mickiewicza 30, 30-059 Krakow, Poland

<sup>2</sup> Łukasiewicz Research Network—Institute of Ceramics and Building Materials, Oświęcimska Street 21, 45-641 Opole, Poland; j.poluszyńska@icimb.pl

\* Correspondence: ekrzeminska@agh.edu.pl

Received: 10 August 2020; Accepted: 11 September 2020; Published: 14 September 2020



**Abstract:** This research involved studying the physico-chemical parameters of fly ash derived from the combustion of 100% biomass in bubbling and circulating fluidized bed boilers of two large energy plants in Poland. Chemical composition revealed that ash contains substantial amounts of CaO (12.86–26.5%); K<sub>2</sub>O (6.2–8.25%); MgO (2.97–4.06%); P<sub>2</sub>O<sub>5</sub> (2–4.63%); S (1.6–1.83%); and micronutrients such as Mn, Zn, Cu, and Co. The ash from the bubbling fluidized bed (BFB) was richer in potassium, phosphorus, CaO, and micronutrients than the ash from the circulating fluidized bed (CFB) and contained cumulatively less contaminants. However, the BFB ash exceeded the threshold values of Cd to be considered as a liming amendment. Additionally, according to our European Community Bureau of Reference (BCR) study Pb and Cd were more mobile in the BFB than in the CFB ash. Except for a low nitrogen content, the ash met the minimum requirements for mineral fertilizers. Acute phytotoxicity revealed no inhibition of the germination and seed growth of *Avena sativa* L. and *Lepidium sativum* plants amended with biomass ash. Despite the fact that low nitrogen content excludes the use of biomass fly ash as a sole mineral fertilizer, it still possesses other favorable properties (a high content of CaO and macronutrients), which warrants further investigation into its potential utilization.

**Keywords:** fly ash; biomass combustion; fluidized bed boilers; acute phytotoxicity test; mineral fertilizer; BCR sequential extraction; metal speciation

## 1. Introduction

Globally, almost one third of electricity is generated from coal; despite this fact, renewable energy sources such as biomass are increasingly gaining a foothold. Twenty-eight European Union (EU) countries are obliged to meet certain targets regarding their share of energy from renewable sources in gross energy production by the year 2020 (according to the EU Directive 2009/28/WE). In 2020, this target is 20% for most EU countries, whereas Poland has to meet a target of 15%. Consequently, the European Environment Agency has indicated that the use of biomass in large combustion plants in the EU has tripled between years 2004 and 2016. For instance, in Poland almost half of the electricity derived from renewable sources comes from biomass. Investments in energy generation derived from biomass are either in the planning stage or have already been implemented in many of Poland's heat and electric power plants.

This investment “boom” has resulted in the generation of an entirely new type of waste. The resultant by-products derived from the combustion of 100% biomass in large power plants as well as power and heat installations are very different from the biomass ash derived from their smaller counterparts. Compared to

conventional fly ash from coal combustion, biomass fly ash has a different composition as well as its own unique characteristics and properties. Therefore, it needs to be stressed that the term “fly ash” should not be regarded as a universal term, since the type of combustion technology as well as type of combustion feedstock (coal, biomass, or biomass co-combustion) generates different types of fly ash. According to the Polish Waste Catalog [1], biomass combustion by-products originating from fluidized bed boilers are classified in the same group as the conventional fly ash from coal combustion (10 01 82). Consequently, this type of waste also undergoes a different utilization pathway than that of other biomass combustion by-products such as fly ash, originating from peat and untreated wood (waste code 10 01 03), or the waste from combusting straw in municipal boilers (10 01 99).

Until now, conventional fly ash, derived from power plants fired with coal fuel, was commonly used for the production of building materials, general-purpose cements, building ceramics, hydraulic binders, and binding materials, and in road construction (road base). The fly ash generated from biomass combustion, due to its unfavorable composition, is not suitable for traditional management methods. For instance, it contains a substantial amount of phosphorus, which slows hydration and extends the setting time of concrete, thus causing a reduction in its strength. However, while this chemical parameter precludes the use of biomass ash in construction materials, still it is a highly desirable attribute in a different utilization direction, such as as a potential mineral fertilizer or soil improver in land use. Fluidized bed boilers are the most commonly recommended type of boiler for combusting biomass fuel, especially in the process of heat and energy production from biomass in large and very large combustion plants. The energy sector uses either bubbling fluidized bed (BFB) technology or its upgraded version, circulating fluidized bed (CFB), sometimes called second-generation boilers. Both combustion technologies are characterized by very high thermal efficiencies of up to 87%, however circulated fluidized bed furnaces are more commonly applied in larger scale power installations. As indicated by Pallarès and Johnsson [2], in BFB technology (referred also as stationary fluidized bed) the combustion mostly takes place in the bed and in the lower part of the freeboard, and there is no external recirculation of the bed, unlike that of CFB boilers, which operate under circulating conditions where, unlike in bubbling beds, combustion is distributed more homogeneously along the height of the furnace. CFB employs a higher gas velocity [3] and/or finer bed solids than those used in BFB.

Biomass combustion by-products are fly ash that is captured by electrostatic precipitators, as well as bottom ash that is collected directly from the grate. Since, in fluidized bed furnaces, sorbents such as ground limestone, dolomite, or lime are used to bind sulfur compounds and control SO<sub>2</sub> emission, the solid residue also contains substantial amounts of desulfurization products, such as calcium sulfate [4]. In order to ensure optimal sulfur binding conditions, the temperature in the furnace chamber is maintained at a level of 850 to 900 °C.

As previously stated, biomass combustion by-products are a very heterogeneous group of waste materials, whose chemical, mineralogical, and physical characteristics vary significantly between installations. Its final chemical composition is influenced by a multitude of factors—i.e., the biomass source and origin, the energy plant's age, the harvesting time, the proportion of biomass/feedstock mixture, the soil and biomass growing conditions, the combustion temperature, the type of sorbent used in the combustion process, or even its granulometry and many other factors [5,6]. Theoretically, the same technological process of combustion and the same feedstock used but delivered from a different source may influence the composition of the final by-product ash. For that reason, it is especially important to characterize each type of biomass ash individually prior to finding an appropriate utilization approach.

Regardless of the occurrence of the great variability of biomass ash—as confirmed, e.g., by Vassilev et al. [6] in their review of almost 600 articles on the topic—the vast majority of researchers agree on the fact that the prevailing types of biomass fly ash derived from both small and laboratory installations [7–9], as well as those from bigger installations such as large or very large fluidized bed boilers [10–13], have good nutritional properties. Researchers report that [14–19], except for its low N

content (which gets volatilized during the combustion process [19]), biomass combustion by-products' chemical composition is similar to that of mineral fertilizers. Despite the fact that this type of waste is nearly free of nitrogen, it contains substantial amounts of other micro (B, Fe, Mo, Mn, Cu, Zn, Co) and macronutrients, both primary (P, K) and secondary (S, Mg, Ca, Na) [20], which are highly favorable in maintaining appropriate conditions conducive for plant growth. Ohenoja et al. [21], for instance, in their broad study on the utilization potential of biomass fly ash where they reviewed at least 46 research papers, confirmed the low content of contaminants in most ash derived from the fluidized bed combustion of pure biomass and satisfactory levels of macronutrients such as phosphorus and calcium, thus concluding the high feasibility of using it as a soil amendment. Moreover, the agronomic effects of using biomass fly ash derived from a variety of feedstocks and combusting technologies on crop yields were also reported by several authors [22–25]. For instance, the P fertilization effects of various biomass ash, such as rape meal ash, cereal ash, or straw ash, on eight types of crops (e.g., as maize, lupin, summer barley, oilseed rape, oil radish, etc.) were evaluated during pot experiments conducted by Schiemenz and Lobermann [15]. The authors concluded that the above-mentioned biomass ash can be an adequate source of phosphorus, even comparable with highly soluble commercial P fertilizers. Furthermore, Meller and Bilenda's findings [26] also confirm the fertilizing potential of biomass fly ash originating from BFB boilers in heat plants, which combust wood and agricultural feedstock. In their in situ experiment conducted on *Miscanthus sacchariflorus* grown on soil fertilized with the addition of BFB fly ash, the authors confirmed that an increased dose of ash caused a significant increase in the amount of available potassium, phosphorus, and magnesium in the soil. They reported that, as a result of amending the soil with  $10.5 \text{ Mg}\cdot\text{ha}^{-1}$  of BFB, the bioavailable phosphorus content in soil was increased by 27.06 mg/100 g, the bioavailable magnesium content by 15.05 mg/100 g, as well as bioavailable potassium by as much as 74.04 mg/100 g. In other research conducted by Ayeni et al. [27], reports of the positive effect of sawdust and wood ash applications on the enhancement of the N and P nutrient content as well as on growth of cocoa seedlings were presented.

In general, the utilization of biomass ash as a soil amendment or fertilizer (field or forest fertilizer) has a long history, especially in Nordic countries. As indicated by Ohenoja [21], Finland, for instance, is an undisputed leader in using this type of waste as a soil amendment. As a result, most research on the utilization potential of biomass ash is also carried out there [20,28–33]. It is a normal utilization practice in Finland to use biomass ash as a sole field or forest fertilizer when it is pretreated (e.g., granulated) and meets the threshold values set for both the contaminant and nutrient content. Both Finland and Denmark have established national legislation dedicated exclusively to ash recycling and fertilizing in forestry [34,35], with set threshold values for the total concentration of detrimental contaminants in ash (As, Cd, Cr, Cu, Ni, Pb, and Zn), as well as the minimum content of nutrients (Ca%, K + K%) required for both field and forest fertilizers. Moreover, the EU theoretically favors the application of biomass ash in top soil, since it fits well into the circular economy approach, however it should be noted that, at the same time, other EU legislation regarding the protection of top soil basically excludes this type of waste for land application, because of the strict limits regarding heavy metal content, which, in some cases, should be considered more as micronutrients than as contaminants. Van Dijen et al. [36] even concludes that EU policies regarding the utilization of biomass ash in agricultural and forest use are contradictory. However, in 2019 the EU recently revised previous fertilizer regulations and delivered a new regulation, (EU) 1009/2019 [37], which will take effect starting from 16 July 2022. This legislation repealing the “old” (EC) No. 2003/2003 regulation [38] will allow and support the general idea of using organic, bio-waste, or recycled fertilizers, such as biomass ash, in top soil as a fertilizer, liming agent, or soil improver alone and in addition to other fertilizing products if the waste has met new limits and threshold values. What is especially important and exceptional in this legislation is that individual EU countries can still set their own national fertilizing legislation with less strict limits, and the EU will still allow these non-conforming products to be available on the market, though not exported as CE products. Consequently, if biomass ash will be suitable and designated for the purpose of top soil

application, it will lose its status as a waste. These are key changes that may act as a springboard, leading to the broader use of this by-product as a soil improver, fertilizer, or liming agent.

The aim of this study was to determine the chemical composition of fly ash resulting from the combusting of 100% biomass in two different types of fluidized bed boiler collected from two very large power plants in Poland (of a capacity of 183 MW and 205 MW), with particular emphasis placed upon the fertilizing properties of ash, as well as content of micro and macronutrients. Moreover, in order to determine the potential toxicity and bioavailability of elements to plants, an aqueous leaching test followed by a three-step sequential extraction European Community Bureau of Reference (BCR) was performed. Furthermore, acute phytotoxicity tests were conducted in order to evaluate the potential influence of the amendment of biomass fly on soil on select plant growth by determining the inhibition of seed germination, the inhibition of root elongation, and ultimately by calculating their germination index. This is the first part of broader research focused on finding the most suitable utilization approach for fly ash from biomass combustion in fluidized bed boilers generated by the Polish large-scale energy sector in millions of tonnes per annum.

## 2. Materials and Methods

### 2.1. Materials

The material in this research consisted of fly ash derived from the combustion of 100% biomass in the fluidized bed boilers of two very large energy plants in Poland. Fluidized bed boilers are the combustion technology employed in both plants.

The first power plant (for the purpose of this research called installation “BFB”) is equipped with Poland’s biggest bubbling fluidized bed boiler (BFB), which has a capacity of 183 MW, whereas the second power plant (for the purpose of this research called installation “CFB”) in turn uses Poland’s biggest circulating fluidized bed boiler (CFB), with a capacity of 205 MW. Both power plants are referred to as “green” installations, since they combust 100% biomass composed of a mixture of wood and agricultural residue (“agro”) feedstock. The addition of “agro” biomass to the total weight of biomass feedstock is mandatory in Poland’s energy production units, which are greater than 5 MW, and its share is strictly regulated. This mandatory inclusion of “agro” biomass (e.g., sunflower husk, different agricultural residues, energy crops, etc.) to the combustion process is quite troublesome. This issues arise from the fact that it has different physico-chemical properties than forest biomass, including particularly high levels of chlorine; sulfur; and alkali metals such as phosphorus, potassium, and sodium, all of which can cause corrosion and other technical problems. All our fly ash samples were collected in 2016/2017, when the minimum addition of “agro” biomass for the purpose of combustion in large “green” power units in Poland was set at a minimum of 20%.

The biomass feedstock in the CFB plant included 80% wood pellets, and the remaining 20% was agricultural waste, which consisted of sunflower husks. The biomass feedstock for the BFB installation consisted of 79% wood pellets, and the remaining 21% was agricultural residue (18% sunflower husks and 3% straw pellets). For further analysis, a total of four samples of fly ash were collected from the electrostatic precipitator, two from each installation. Samples of 20 kg each were homogenized, averaged, and determined to be representative for further analysis and tests.

### 2.2. Methods

The chemical composition of all fly ash samples was determined via X-ray fluorescence, using a WD-XRF ZSX Primus II Rigaku Spectrometer. Qualitative spectrum analysis was performed by identifying spectral lines, determining their possible coincidences, and then selecting analytical lines. The semi-quantitative analysis was conducted using the SQX Calculation program (fundamental parameter method), and was carried out in ranges from fluorine to uranium (F-U). Furthermore, the content of the determined elements was then normalized to 100%. Prior XRF analysis samples were prepared using a standard pelleting technique with the addition of a binder (Celleox) in a 4:2 proportion.

The concentration of chloride in ash was additionally determined using the titration method according to the European standard EN 196-2:2013 [39]. In order to determine the total concentration of metals in fly ash, samples were extracted with conc. nitric acid and hydrogen peroxide using microwave oven PRO, Anton PAAR, following digestion protocol PN-EN 13,657:2006 [40]. Furthermore, the concentrations of metals V, Cr, Mn, Co, As, Cd, Sn, Sb, Tl, and Pb were then analyzed via ICP-MS (Agilent 7700x) according to PN-EN ISO 17294-2:2016-11 [41]. The detection limits for particular elements in the ICP-MS apparatus were 0.25–2500 mg/kg. Mercury in raw samples was measured using atomic absorption spectrometry with amalgamation (AMA 254), according to an L-ICIMB accredited procedure: PB-LL-10 ed. 2 of 04/09/2017. The detection limits for this analytical device ranged from 0.005 to 100 mg/kg. The nitrogen and sulfur content was determined using the elemental analyzer CHNS + Cl + O Vario MACRO Cube by Elementar, using a high-temperature combustion method with TCD detection. Measurements were conducted according to PN-EN 15407:2011 [42] for N and PN-EN 15408:2011 [43] for S. The detection limits of the elemental analyzer device for N were 0.05–10% and were 0.1–8% for S. The primary nutrients in fly ash (P, N, K, S, Mg, Na, Ca) were expressed in both elemental as well as oxide forms, as requested by the EU fertilizer legislation act (EC) No. 2003/2003 [38], using the following conversion values: phosphorus (P) = phosphorus pentoxide ( $P_2O_5$ )  $\times$  0.36; potassium (K) = potassium oxide ( $K_2O$ )  $\times$  0.830; calcium (Ca) = calcium oxide (CaO)  $\times$  0.715; magnesium (Mg) = magnesium oxide (MgO)  $\times$  0.603; sodium (Na) = sodium oxide ( $Na_2O$ )  $\times$  0.742; (d) sulfur (S) = sulfur trioxide ( $SO_3$ )  $\times$  0.400.

Furthermore, a 24 h aqueous leaching test was conducted in order to determine the toxicity and thus potential mobility and bioavailability of elements in fly ash, according to PN-EN 12457-2006 [44]. This simple one-step test consisted of leaching ash for 24 h with distilled water in the ratio of 10:1 water to dry weight of the sample. The concentrations of chloride, sulfate, nitrate, and phosphate anions in the leachates were then determined according to PN-EN ISO 10304-1:2009/AC 2012 [45], and the concentrations of sodium, potassium, calcium, and magnesium cations were detected according to PN EN ISO 14911:2002 [46] using the ion chromatography method (Metrohm IC 850 Professional with a conductometric detector and UVVIS). The concentration of the “leachable” and easily soluble metals, such as V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sn, Tl, and Pb, were then determined using the ICP-MS method. A more appropriate study on the bioavailability of primary nutrients—that is, potassium and phosphorus—was then conducted using the calorimetric method ( $P_2O_5$ ), as well as the flame photometric method ( $K_2O$ ). The available phosphorus content in ash was determined in accordance with PN-R-04023:1996 [47] using the MERCK SQ118 calorimeter. The content of bioavailable potassium was determined in accordance with the PN-R-04022: 1996/A1: 2002 [48] using the Zeiss flame photometer.

A speciation study of all the fly ash was performed using the 3-step sequential extraction proposed by the European Community Bureau of Reference (BCR), and delivered as a standardized and improved method of sequential extraction, mainly the commonly used 6th-step extraction according to Tessier et al. [49].

The dried ash samples (1 g, 2 h at 105 °C) were subjected to 3-step extraction according to the procedure provided by Ure et al. [50], included in Table 1. Samples were subjected to each extraction step using solutions of increasing aggressiveness in order to extract metals associated with individual fractions—that is, (step 1) the acid-soluble fraction, associated with exchangeable metals and bound with carbonate; (step 2) the reducible fraction, associated with metals bound to iron and manganese oxides; (step 3) the oxidizable fraction, including metals bound to organic matter and sulfides. After each extraction stage, the obtained residue was rinsed with deionized water, centrifuged, and subjected to another stage of extraction. In order to control the quality of the obtained results, an additional step was introduced to this procedure, which consisted of the digesting of ash with 10 mL of 65%  $HNO_3$  and 2 mL of  $H_2O_2$ . The concentrations of metals in all the extracts were determined via ICP-MS.

**Table 1.** BCR speciation protocol.

Extraction Step	Fraction	Extractant
I	Acid soluble: exchangeable metals bound with carbonates.	0.11 M CH <sub>3</sub> COOH S/L = 1:40 16 h shaking 30 rotation/min
II	Reducible: metals bound to Fe and Mn oxyhydroxides.	0.1 M NH <sub>2</sub> OH·HCl, pH 2 (HNO <sub>3</sub> ) S/L = 1:40 16 h shaking 30 rotation/min 30% H <sub>2</sub> O <sub>2</sub> per 1 h, then
III	Oxidisable: metals bound to organic matter and sulfides.	1M CH <sub>3</sub> COONH <sub>4</sub> , pH 2 (HNO <sub>3</sub> ), S/L = 1:50 16 h shaking 30 rotation/min
IV *	Residual: lithogenous, non-silicate bound metals.	65% HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>

\* Additional and recommended step.

The quality of the obtained results of all analyses was ensured by performing them according to a standard certified analytical quality control procedure according to PN-EN ISO 17294-1:2007 [51]. In order to further ensure the quality of the results obtained, reagent blanks and certified reference material (fly ash from pulverized coal, BCR 038) were used (including BCR protocol). The analytical bias was found to be statistically insignificant ( $p = 0.05$ ). The uncertainty of the obtained results is provided in Tables 2 and 3.

**Table 2.** Chemical composition of fly ash from biomass combustion in fluidized bed boilers.

Parameter	Fly Ash from CFB 1	Fly Ash from CFB 2	Fly Ash from BFB 1	Fly Ash from BFB 2	Threshold Values for Mineral Fertilizers (mg/kg) *	Minimum Nutrient Content for Mineral Fertilizers (wt%) *
V	22.6 ± 8.9	24.8 ± 9.7	14.3 ± 5.6	18.9 ± 7.4	-	-
Cr	50.0 ± 20.8	44.5 ± 18.5	48.5 ± 20.1	53.6 ± 22.2	-	-
Mn	2315 ± 801	2299 ± 795	5698 ± 1972	7157 ± 2476	-	-
Co	6.17 ± 2.42	5.31 ± 2.09	4.31 ± 1.69	4.72 ± 1.85	-	-
Ni	33.8 ± 10.9	27.2 ± 8.8	17.3 ± 5.6	21.0 ± 6.8	-	-
Cu	112 ± 38	92.9 ± 31.7	146 ± 50	86.8 ± 29.6	-	-
Zn	325 ± 131	337 ± 135	583 ± 234	593 ± 238	-	-
As	15.9 ± 4.9	6.41 ± 1.99	6.82 ± 2.12	7.85 ± 2.44	50	-
Cd	6.12 ± 2.01	6.10 ± 2.00	8.14 ± 2.67	8.15 ± 2.67	50 */8 **/5 ***	-
Sn	7.50 ± 2.85	3.63 ± 1.38	1.02 ± 0.39	b.d.l.	-	-
Sb	2.25 ± 0.68	2.67 ± 0.81	0.050 ± 0.015	0.800 ± 0.242	-	-
Tl	1.15 ± 0.42	0.945 ± 0.347	2.11 ± 0.77	2.90 ± 1.06	-	-
Pb	129 ± 45	71.3 ± 24.7	61.7 ± 21.4	51.4 ± 17.8	140 */200 **/600 ***	-
Hg	0.086 ± 0.023	0.064 ± 0.017	0.220 ± 0.059	0.240 ± 0.064	2	-
P <sub>2</sub> O <sub>5</sub>	2.00 ± 0.40	2.38 ± 0.48	3.57 ± 0.74	4.63 ± 0.93	-	2
P	0.880	1.04	1.57	2.04	-	-
K <sub>2</sub> O	6.20 ± 0.37	6.88 ± 0.41	6.62 ± 0.40	8.24 ± 0.49	-	2
K	5.14	5.71	5.49	6.84	-	-
CaO	12.9 ± 2.3	14.1 ± 2.5	26.5 ± 4.8	24.8 ± 4.5	-	-
Ca	9.19	10.06	18.94	17.73	-	-
MgO	3.77 ± 0.45	4.06 ± 0.49	2.97 ± 0.36	3.31 ± 0.40	-	-
Mg	2.27	2.45	1.79	1.99	-	-
SO <sub>3</sub>	4.59 ± 0.92	3.97 ± 0.79	4.16 ± 0.83	4.53 ± 0.91	-	-
S	1.84 ± 0.18	1.59 ± 0.16	1.66 ± 0.16	1.81 ± 0.18	-	2
N	0.040 ± 0.004	0.030 ± 0.003	0.020 ± 0.002	0.020 ± 0.002	-	-
Cl	1.54 ± 0.16	1.16 ± 0.12	1.42 ± 0.15	1.32 ± 0.14	-	-
pH					-	-
PEW (mS/m)	12.07	10.5	20.4	18.77	-	-

\* Max. concentration of contaminants in mineral fertilizers according to Dz.U.119.765 [59]; \*\* max. concentration of contaminants in fertilizing lime (liming agent) 8 mg of Cd per 1 kg of CaO, 200 mg of Pb per 1 kg of CaO; \*\*\* max. concentration of contaminants in fertilizing lime containing magnesium 5 mg Cd per 1 kg of CaO + MgO, 600 mg Pb per 1 kg of CaO + MgO. b.d.l.—below detection limit of the analytical device (for the V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sn, Sb, Tl, Pb detection limit for ICP-MS ranges between 0.25 and 2500 mg/kg).



**Table 3.** Leachability of the elements from biomass ash.

Leachable Concentration of Elements	Fly Ash from CFB 1	Fly Ash from CFB 2	Fly Ash from BFB 1	Fly Ash from BFB 2
V	b.d.l.	b.d.l.	0.0035 ± 0.0013	0.0022 ± 0.0008
Cr	5.5 ± 1.46	5.2 ± 1.37	4.46 ± 1.19	4.99 ± 1.33
Mn	0.01 ± 0.002	0.032 ± 0.0064	0.037 ± 0.0079	0.043 ± 0.0092
Co	b.d.l.	b.d.l.	0.0022 ± 0.00053	0.0015 ±
Ni	0.5 ± 0.086	0.4 ± 0.068	0.066 ± 0.0114	0.0136 ± 0.0023
Cu	b.d.l.	b.d.l.	0.385 ± 0.073	0.074 ± 0.0141
Zn	0.21 ± 0.076	0.36 ± 0.13	0.59 ± 0.135	0.75 ± 0.169
As	0.09 ± 0.033	0.05 ± 0.018	0.036 ± 0.00131	<0.001
Cd	b.d.l.	b.d.l.	<0.001	0.00079 ± 0.00021
Sn	0.12 ± 0.0316	b.d.l.	<0.001	<0.001
Tl	b.d.l.	b.d.l.	0.0148 ± 0.0049	0.0361 ± 0.0118
Pb	0.04 ± 0.010	0.0352 ± 0.009	0.602 ± 0.155	0.715 ± 0.184
Cl <sup>−</sup>	13,168 ± 1027	10,439 ± 814	12,230 ± 954	14,850 ± 1158
SO <sub>4</sub> <sup>2−</sup>	18,200 ± 3585	27,720 ± 5461	23,320 ± 4594	27,170 ± 5352
PO <sub>4</sub> <sup>3−</sup>	b.d.l.	b.d.l.	b.d.l.	b.d.l.
NO <sub>3</sub> <sup>−</sup>	147 ± 11	152 ± 11	140 ± 10	146 ± 11
Ca <sup>2+</sup>	6209 ± 1130	4411 ± 803	6940 ± 1263	6135 ± 1117
Mg <sup>2+</sup>	339 ± 40	88.8 ± 10.4	0.200 ± 0.023	0.200 ± 0.023
Na <sup>+</sup>	97.4 ± 11.3	39.7 ± 4.6	87.6 ± 10.16	44.7 ± 5.18
K <sup>+</sup>	38,842 ± 2447	23,036 ± 1451	29,864 ± 1881	32,989 ± 2078
K <sub>bioavailable</sub> (K <sub>2</sub> O)	4043	3520	3750	3000
P <sub>bioavailable</sub> (P <sub>2</sub> O <sub>5</sub> )	2.5	1.8	2.1	2.2

b.d.l.—below detection limit.

The acute phytotoxicity test (Phytotoxkit, Tiger MicroBioTest) was employed in order to determine the possible or potential inhibition of the seed germination, IG [%], as well as the inhibition of the root elongation, IR, as a result of soil amended with fly ash. These types of plant germination tests are commonly used by other researchers [52–56] to determine the toxicity of certain substrates (such as fertilizers, sludge, compost, waste, or other soil amendments) on the root elongation of terrestrial plants after a specific time of exposure to a certain soil contaminant when compared to control soil. The methodology used in the study was in line with ISO Standard 11269-1: 2012 [57]. OECD soil (series no: OERS011217) was used as a control and reference sample. Seeds of monocotyledonous (*Avena sativa* L.) and dicotyledonous (*Lepidium sativum*) plants were selected for the test in accordance with the OECD/OCDE guidelines 208/2006, which state that it is necessary to conduct research on plants from various systematic units.

The ash additive to OECD soil was calculated as 2.5 tonnes of CaO amendment per hectare for a 0.25 m depth of soil. Ten seeds of indicator plants were sown both in the experimental trials and in the control sample, as described in the phytotoxic test method. Calculations were also made in accordance with the test instructions. All the tests were performed in 3 replications.

Seeds of a selection of plants were laid on a paper filter lying on the surface of moistened soil/soil with fly ash. The plates were enclosed and then placed vertically and incubated at 25 °C in a thermostatic cabinet in the dark for 5 days. After the incubation, digital photographs of the incubated plates were taken, the number of germinated seeds was counted, and the root length of the germinated plants was measured. Finally, the inhibition of seed germination IG [%], the inhibition of root elongation IR in soil [%], as well as the GI germination index were calculated according to the following equations:

$$\frac{G_A - G_B}{G_A} \times 100 = IG \text{ [%]}$$

where:

$G_A$ —average number of seeds germinating on control soil (OECD);

$G_B$ —average number of seeds germinating on experimental medium.

$$\frac{R_A - R_B}{R_A} \times 100 = IR [\%]$$

where:

$R_A$ —average root length on control soil (OECD);

$R_B$ —average root length on experimental medium.

$$\frac{G_B \times R_B}{G_A \times R_A} \times 100\% = GI$$

### 3. Results and Discussion

#### 3.1. Physico-Chemical Properties of Fly Ash from Biomass Combustion in Fluidized Bed Boilers

The chemical compositions of fly ash from both installations as well as its physical parameters are presented in Table 2. All the examined fly ash was alkaline, and the pH varied between 10.7 and 13.07, however the samples from the BFB installation were more alkaline than those of the CFB plant. The electrical conductance was reported to be high in all samples, however fly ash from the bubbling fluidized bed was twice as conductive (18.77–20.4 mS/cm) as samples taken from the circulating fluidized bed (10.05–12.07 mS/cm). These results are consistent with the findings of other researchers reporting a strongly alkaline pH of biomass ash delivered from large-size installations. Dahl et al. [28] reports that the pH of biomass ash delivered from a 246 MW fluidized bed boiler was found to be in the 11.9 to 12.6 range; Uliasz-Bocheńczyk et al. [58] reported biomass ash to have a pH even more alkaline (pH 12.92). Żelazny and Jarosiński [13], in their research on evaluating the biomass ash from Połaniec (205 MW) energy plant as a possible fertilizer, also confirm that the pH of biomass ash was highly alkaline, at pH > 11, and they concluded that such conditions may promote a significant loss of ammonia and phosphorus from NPK biomass fertilizer, as a result of the decomposition of ammonia from the nitrate ammonia compound and the formation of phosphorus compounds insoluble in water. In regard to the conductivity, Wilczyńska-Michalik et al. [12], in their research on biomass fly ash from the same 205 MW energy plant as ours, reveal a comparable conductivity which is equal to 11.38 mS/cm.

#### 3.2. Macro and Micronutrient Contents in Biomass Fly Ash in Accordance with Fertilizer Legislation

All the fly ash samples derived from both installations contained a substantial number of elements, macronutrients (P, K, S, Ca, and Mg), and micronutrients (Mn, Cu, Zn, Co) considered as being essential for plant growth. The concentration of nitrogen, however, in all the evaluated samples was negligible, and it varied from 0.02% to 0.04%. These results correspond with the outcomes of other authors reporting a low level of nitrogen in biomass fly ash obtained from a variety of feedstock and combustion technologies [59–61]. It can therefore be concluded that none of the examined biomass fly ash from fluidized bed boilers met the minimum 2% nitrogen content threshold required for mineral fertilizers, in accordance with Polish legislation [59]. The concentrations of the remaining macronutrients, such as K and P, were satisfactory. However, when considering EU legislation regarding fertilizers [38], it was found that here the content of K and P were to meet the minimum requirements for K fertilizers (i.e., min. 10% of soluble  $K_2O$ ), for PK fertilizers (min. 18% of  $P_2O_5 + K_2O$ ), as well as for NPK fertilizers (min 20% of  $N + P_2O_5 + K_2O$ ). The results are then in agreement with the findings of Żelazny and Jarosiński [13], who conclude that the sole use of this type of waste as a full-value fertilizer is not possible; however, this waste could be considered as a source of potassium for the purpose of a more complex type of fertilizer (NK, PK, or NPK) production.

The fly ash from our BFB power plant was richer in potassium, phosphorus, and CaO than the ash delivered from our CFB power plant. The BFB fly ash contained two times more phosphorus (mean con. of 1.8% P) than ash from the CFB plant (mean con. of 0.96% P). It also contained two times



more CaO (on average, 25.65% CaO compared to 13.46% in CFB) and had a higher level of potassium (7.43% K<sub>2</sub>O in BFB fly ash, compared to 6.54% K<sub>2</sub>O in CFB). The MgO and sulfur content remained comparable for both the BFB and CFB fly ash. The higher content of P and K in fly ash from the BFB could be the result of incinerating a higher share of “agro” biomass (21% agro addition) in the BFB boiler compared to the CFB installation, which incinerated only a 20% mix of “agro” bio. Moreover, the “agro” biomass used by the BFB boiler consisted of a mixture of sunflower husks (18%) and an additional 3% straw pellets. Straw, according to the results of various authors [62,63], appears to be richer in K and P content than sunflower husks alone.

Comparing our results with the findings of Wilczyńska-Michalik et al. [12], it can be safely concluded that the macronutrient content is mostly convergent, especially with regard to P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O. However, the concentration of CaO as well as S in the CFB fly ash differed more significantly compared to both findings. For the fly ash samples CFB1 and CFB2, the concentration of CaO ranged from 12.86 to 14.07 wt%, which was found to be lower than the CaO concentration reported by Wilczyńska-Michalik et al. [12] (18.56 wt% CaO). On the other hand, the fly ash examined during our study was richer in sulfur content (1.58–1.83 wt%) than the fly ash examined by Wilczyńska-Michalik et al. [12] (1.12 wt%). The differences in the macronutrient content between both studies can probably be attributed to a different biomass feedstock mixture being incinerated in the same power plant. However, further comparison is difficult due to the lack of detailed information regarding the type of biomass used and its composition (especially undefined by the authors is the 20% agricultural feedstock addition).

The results of the macronutrient content of fly ash from BFB boilers were then referenced with the results of other researchers studying biomass ash obtained under comparable technological conditions. For example, Nurmesniemi et al. [20], who studied fly ash originating from large BFB power plant (115 MW) boilers, when incinerating clean forest biomass with an addition of 3% wastewater sludge reported comparable contents for Ca and P but a lower content of Mg 1.79–1.99% and a lower sum of P + K compared to the results obtained from our study performed on samples taken from a BFB installation. Our findings on the macronutrient composition of BFB ash revealed substantially more K (5.49–6.84 % mass) compared to the 3.9% reported by Nurmesniemi et al. [20], and even three times more CaO, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> compared to the results reported by Wilczyńska-Michalik et al. [12], which they obtained by studying a much smaller (76.5 MWt) BFB installation and incinerating 100% agricultural residues.

A broader comparison of our results with the findings of other researchers [6–8,12,15,60,61] studying a multitude of fly ash from a variety of biomass feedstock and installations confirms that biomass incineration by-products are a quite heterogeneous type of waste. For instance, in the very broad research conducted by Zajac [7], it was found that the nutritional composition of fly ash derived from burning wood biomass, energy crops, agricultural biomass, and forest and agri-food industry waste varies significantly depending on the feedstock used (e.g., the P content (wt%) varied from 0.26 to 3.2, the K (wt%) varied from 1.9 to 18.7, and the Ca (wt%) varied from 3.6 to 35).

In our research, a high content of chlorine was found in both types of ash (1.16–1.54 wt%), which, according to Jaworek et al. [64], is a characteristic “trade mark” of bio-ash compared to coal fly ash.

The total concentrations of macronutrients in the fly ash of this study decreased in the descending order of nutritional elements Ca > K > Mg > S > P > N. Detailed results of this composition are depicted in Table 2. The concentrations of individual macronutrients ranged from 0.88% to 2.04% for P, 5.14–6.84% for K, and 0.02–0.02% for N, as well as 1.58–1.83% for S, called “the fourth macroelement”. The concentration of micronutrients, on the other hand (Mn, Cu, Zn, Co), varied more significantly within different types of fly ash, especially with regard to the manganese content, ranging from 2299 up to 7157 mg/kg. The concentration of this essential nutrient (Mn) was three times higher in fly ash from the BFB than that of the fly ash from the CFB installation. Similarly, the concentration of Zn in the fly ash from the BFB was found to be twice as high as that of the CFB fly ash, on average 588 mg/kg Zn and 331 mg/kg, respectively. The concentrations of the remaining micronutrients, such as Co and Cu, in ash was comparable and varied insignificantly between the two installations. After comparing

the obtained micronutrient content results with the findings of Wilczyńska-Michalik et al. [12] for the same installation (205 MW), it was determined that our outcomes are in line with one another.

### 3.3. Non-Essential Elements and Contaminants

Besides nutritional elements, biomass fly ash waste also contains metals (V, Cr, Ni) that are non-essential for plants but at the same time could be considered beneficial for their growth when introduced in small amounts. For instance, Vanadium is not an essential element for plants, however it can stimulate growth and chlorophyll formation when added in small quantities [65]. At the same time, this metal can also be toxic to plants when present in elevated concentrations. Some authors [66] report that the addition of Vanadium to flovo-aquic soil in amounts exceeding 30 mg/kg significantly decreases the yields of shoots and roots. The concentration of Vanadium did not exceed 24.8 mg/kg in all the examined fly ash obtained from both the CFB and BFB installations. However, since those values for V concentrations are not so far apart, further research on that issue should be conducted.

Chromium is also a non-essential element which is potentially detrimental to plants, causing oxidation stress and initiating the degradation of photosynthetic pigments, consequently resulting in a decline in plant growth. Although conversely, as indicated by Shanker [67], Cr can actually enhance the growth of certain plant species at lower concentrations. The concentration of Cr in the fly ash of our study was not elevated and was comparable between the two installations, and it was not elevated, varying between 44.5 and 53.6 mg/kg. The content of this element was thus much lower than, e.g., that obtained by Schiemenz and Eichler-Löbermann [15] for rape meal ash derived from laboratory fluidized bed combustion. Although the concentrations of Cr and Ni are not specified by fertilizer legislation, it is noteworthy to point out that, in all of the studied biomass ash samples, the concentrations of these heavy metals were not elevated and were found to be within the upper threshold values established for the 1st quality soil group in accordance with Polish legislation [68]. Similarly, the concentration of Ni was rather low, and thus did not exceed the threshold values established for type 1 classification. It ranged from 17.3 mg/kg in the fly ash from BFB up to 33.8 mg/kg for the CFB fly ash. Therefore, fly ash from both types of fluidized bed boilers should be regarded as not potentially harmful to plants' growth with regard to V, Cr, and Ni contamination.

Biomass fly ash also contains highly phytotoxic elements which do not play any role in plant metabolism and are simply considered as contaminants (As, Cd, Pb, Sb, Tl, and Hg). These metals are not biologically essential for plants, and they are highly phytotoxic at certain threshold values. The maximum permissible levels of As, Cd, Pb, and Hg in mineral fertilizers are regulated by appropriate legislation [59]. All of the examined fly ash samples did not exceed the threshold values established by the above-mentioned regulation regarding the content of contaminants. The concentration of As in the samples ranged from 6.41 to 15.9 mg/kg, thus not exceeding the 50 mg/kg limit. Furthermore, the fly ash samples contained a low level of Cd, ranging from 6.1 to 8.15 mg/kg; Pb, ranging from 51.4 to 129 mg/kg; Sb, ranging from 0.05 to 2.67 mg/kg; and Tl, ranging from 0.94 to 2.9 mg/kg, as well as a low concentration of Hg, ranging from 0.086 mg/kg in the CFB ash to 0.24 mg/kg in the ash delivered from the BFB installation. However, after comparing the above concentrations with the threshold values established for liming agents (fertilizing lime and fertilizing lime containing magnesium), it can be concluded that only fly ash from the circulating fluidized bed installation can legally be used as a direct soil liming amendment, whereas the content of Cd (8.14–8.15 mg/kg) in the ash from the bubbling bed exceeds both the maximum permissible concentrations of 8 mg of Cd per 1 kg of CaO as well as 5 mg of Cd per 1 kg of CaO + MgO.

On the other hand, when considering the cumulative concentration of elements in ash regarded as contaminants (As, Cd, Pb, Hg, Tl, and Sb), as well as toxic and non-essential elements (such as V, Cr, and Ni), it was found that the fly ash derived from CFB installations is more contaminated with metals than the fly ash derived from the BFB installation. The cumulative concentration of metals in the CFB samples reached an average of 227.9 mg/kg, and an average of 162.2 mg/kg in the BFB samples.

A comparison of our results with those presented by Wilczyńska-Michalik et al. [12] for the same installation revealed that, while the contents of Co, Ni, and Cu in the CFB fly ash from both studies were comparable, the results of the concentrations of Cr, Cd, Tl, and Pb varied greatly, by as much as three-fold, depending on the metal. For example, the fly ash obtained by Wilczyńska-Michalik et al. [12] was much more contaminated with Cr and Cd. Furthermore, they reported a Tl concentration 10 times lower and a Pb content three times lower than the ones observed in this study. This was the case despite all the samples originating from the very same circulated bed boiler installation. However, as previously stated the above-mentioned variations in our study compared with that of Wilczyńska-Michalik et al. [12] may result from using a different mixture of biomass feedstock for the incineration process in the CFB power plant, or may even be attributed to using different metal digestion protocols. It has to be noted that different ash mineralization protocols, employing various extraction liquids and various equipment, can greatly influence the recovery rates of metals from fly ash.

The BFB ash results were mostly consistent with the findings of other researchers, such as Dahl et al. [28] and Nurmesniemi et al. [20,31], who conducted similar studies on the content of metals in fly ash derived from large-size BFB installations in Finland (296, 246, and 115 MW). Comparing their outcomes with the results of this study on BFB ash from a 183 MW installation, some conclusions may be drawn. The first is that the BFB1 as well as BFB2 samples of fly ash contained substantially less contaminants such as Cr and As. Second, more Cd and Zn was, however, determined in our BFB ash compared to the fly ash originating from large power plants in Finland (115, 246, and 296 MW) [20,28,31].

### 3.4. Bioavailability of Elements from Fly Ash

The total concentration of metals in fly ash does not deliver sufficient information on the real mobility and bioavailability of these elements. The bioavailability of metals in the soil–plant environment is a very complex issue governed by multiple factors, such as the pH; redox potential; organic content of the substrate; total content of metals; speciation; concentration of organic and inorganic ligands, including humic and fulvic acids; soil texture; clay content; microbial activity; or simply the coexistence of synergetic or antagonistic metals. In such a complex substrate as soil, most of all the above-mentioned factors are interrelated and can vary in wide ranges. Metals considered as both macro and micronutrients, unlike organic matter, are not metabolically degradable, and by changing their chemical forms from soluble to insoluble (due to the above-mentioned factors), they can stay in the ecosystem for tens or even hundreds of years [69–72].

Considering the fact that metals in the fly ash are not permanently fixed, an extended study on the bioavailability of elements using aqueous leaching tests as a well speciation study, based on three-step sequential extraction proposed by the European Community Bureau of Reference (BCR), was deemed necessary. A one-stage aqueous leaching test was chosen because it is most commonly used to pre-characterize the toxic effect of the substrate and to deliver preliminary information on easily soluble forms of metals in ash. Sequential extraction protocols were further used to broaden the scope of the research by providing information on the main phases of metals in which the metals are bound in ash, thus delivering results on its potential anthropogenic and lithogenic origin. The potential mobility of the trace elements in all the examined fly ash is summarized in Table 3.

The aqueous leaching test revealed the enhanced leachability of sulfate ions for all fly ash samples, ranging from 18,200 up to 27,720 mg/kg. Such a high mobility of sulfates is a consequence of the ash composition, which also contains a substantial amount of waste gypsum, a by-product of the desulfurization process which is incorporated in the waste stream during fluidized bed combustion. Elemental sulfur is absorbed by plants when oxidized to sulfate ions. This element in its bioavailable form is highly favorable in all fertilizers, since sulfur is essential for plant growth and functioning [73,74], it provides proper nutrition for plants, resulting in increased yields, and improving their quality [75]; it is responsible for the resistance of plants to biotic and abiotic stresses; and governs and controls proper

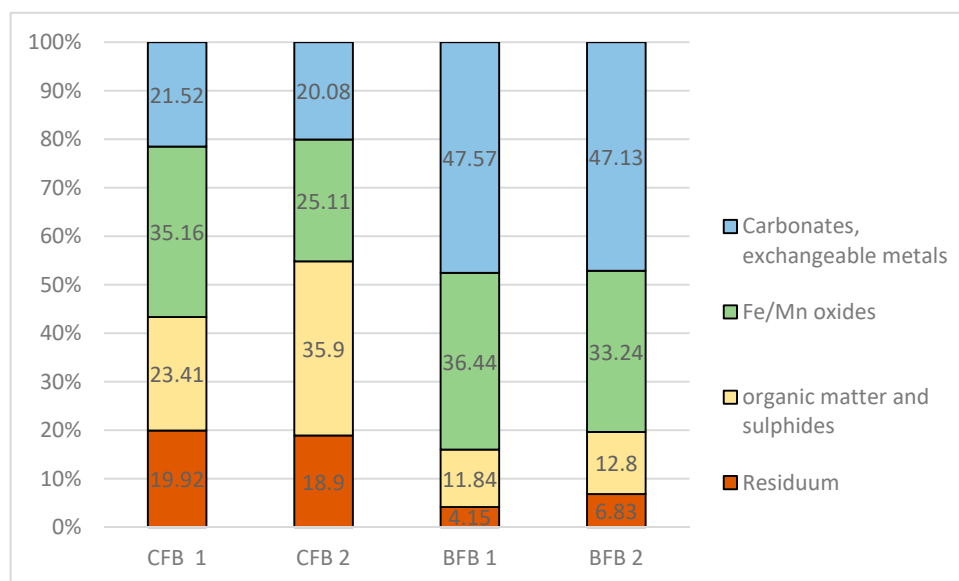
nitrogen metabolism. Thus, when properly supplemented, it allows a reduction in the applied doses of nitrogen fertilizers. A very high content of chloride anions ranging from 10,440 to 14,850 mg/kg was also found in all the fly ash leachates from both installations. Chloride is an essential micronutrient to plants, but only in small amounts. However, when it appears in such extreme concentrations of chloride anions, as found in both types of fly ash, it can be potentially detrimental to plants, causing salinity stress and thus a reduction in yield, water uptake, or photosynthetic capacity due to chlorophyll degradation [75]. At the same time, it should be stressed that chloride and sulfate anions are antagonistic, so the excess of one anion can cause the limited availability of another anion in fly ash. Leaching tests results also revealed the high mobility and bioavailability of other macronutrients, such as potassium (23,030 to 38,840 mg/kg) and calcium (4410 to 6940 mg/kg).

Vassiliev et al. [5] reports that the high leachability of Cl, S, or Ca from biomass ash may result from the content of highly soluble chlorides, such as sylvite; halite; sulfates (e.g., ettringite, gypsum, anhydrite, etc.); or carbonates, such as calcite, dolomite, etc.

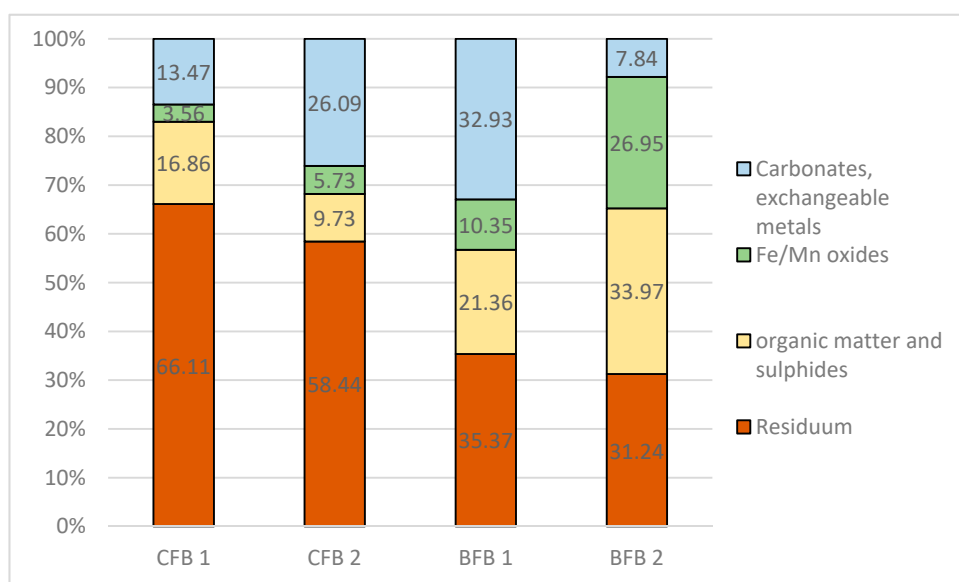
A relatively low mobility of magnesium was reported, varying from 2 to 330 mg/kg, as well as a negligible amount of easily soluble phosphates when compared to their total content in the ash. It has to be noted that phosphorus is available for plants in various forms, including active phosphorus (present in the soil solution in the form of phosphoric acid dissociation ions), mobile phosphorus (i.e., its compounds are soluble in weak acids), and “spare” phosphorus (in the form of various types of apatites). Total phosphorus, then, is the sum of all its above-mentioned forms. The leaching test results revealed a lack of active and easy soluble phosphorus in ash, undetectable using the IC method. More accurate research on other mobile and bioavailable forms of this element in fly ash (including both organic and inorganic forms) was conducted for this reason. The concentration of bioavailable phosphorus determined using the Egner–Riehm method was rather low in all the samples and ranged from 2.0 to 2.2 mg/100 g of  $P_2O_5$  (20–22 mg/kg). Our results are therefore consistent with the findings of other authors [15,20,76,77] reporting the poor water solubility and bioavailability of phosphorus from biomass ash to plants. However, as indicated by Schiemenz and Eichler-Löbermann [15], the bioavailability of phosphorus is governed mainly by the soil pH, so the better solubility of calcium phosphates under acidic pH conditions can enhance the effect of biomass ash. The low water solubility of phosphorus should also be regarded as a positive outcome, since it limits the risk of the uncontrolled leaching of this element from the ash to the soil when considered as a soil amendment for forestry use. The remaining trace metals—V, Mn, Co, Zn, Tl, Pb, and As—in both types of fly ash were also poorly soluble in water, and their concentrations in leachates did not exceed 1% when compared to the total content of metals in ash. The only exception was Cr, which was leached out from both types of ash (CFB and BFB) in amounts accountable for about 10% of its total content in each fly ash sample. Detailed results from the aqueous leaching test are provided in Table 3.

### Speciation of Metals in Fly Ash

A BCR speciation study was conducted with the use of more aggressive sets of reagents in order to reveal information about Cd, Zn, and Pb binding forms in certain types of fly ash and their probable origin. Detailed results are depicted in Figures 1–3.



**Figure 1.** Speciation of cadmium in fly ash.



**Figure 2.** Speciation of Pb in fly ash.

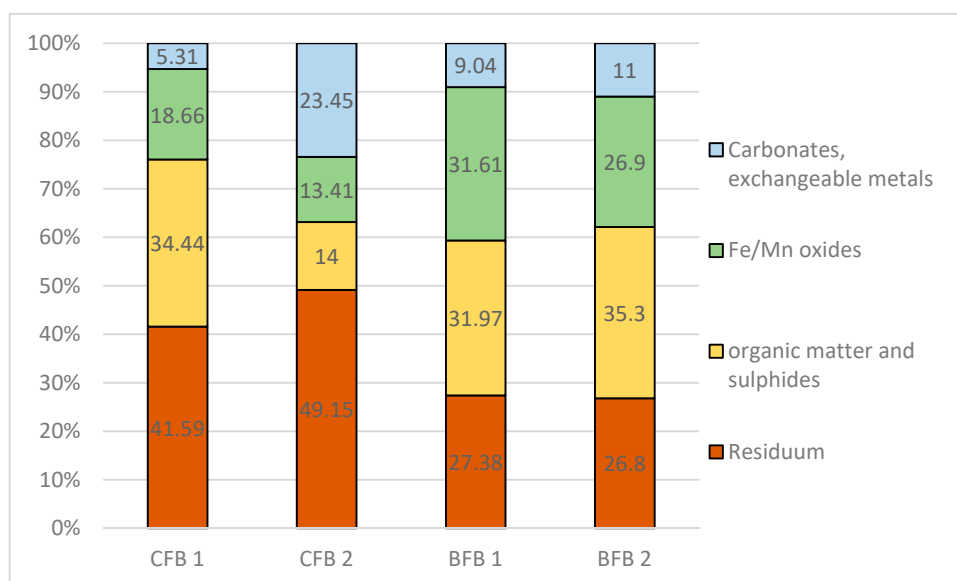


Figure 3. Speciation of Zn in fly ash.

The cadmium contents in individual fractions of both CFB and BFB fly ash differ within samples. In the fly ash from the CFB, cadmium was bound with all three fractions almost in equal amounts; however, in ash CFB 1 this metal was associated mostly with reducible fractions of amorphous Fe/Mn oxides (35%), whereas in the second sample of ash, CFB2, delivered from the same installation, Cadmium was predominantly bound with the oxidizable fraction, not susceptible to leaching and associated with organic matter and sulfites, as well as with the mineral residuum phase (total of 54.8%). In both samples of fly ash from the CFB installation, about 20–21% of the cadmium was bound with the labile and acid soluble phase associated with carbonates, from which metals can easily be remobilized under, e.g., the dropping of pH. In the fly ash collected from the bubbling bed installation, cadmium was much more mobile and potentially bioavailable, since the prevailing amount of this element was bound with easily exchangeable fractions (about 47%), as well as with the reducible phase (about 33% to 36% of Cd). As indicated by the authors [78–80], the reducible fraction acts as a sink to contaminants because Fe/Mn oxides are present as coatings on mineral surfaces or clay particles in the soil matrix, and consequently contaminants can be remobilized from that phase under redox conditions. Consequently, only about of 4% to 6% of the cadmium was then immobile and fixed with the residuum, and about 12% of the Cd was associated with the oxidizable phases of organic matter and sulfides.

Conducting a fractionation study revealed that the prevailing amount of lead (58–66%) in both samples of CFB fly ash is not bioavailable, since it is bound in the residual fraction, while 10% to 17% of this element is also associated with organic matter and sulfides. This indicates that lead still can be potentially released under oxidizing conditions. To the smallest extent (3.56–5.73%), the lead in CFB ash is bound with the reducible fraction associated with Fe/Mn oxides, and it can be susceptible to release under reducible conditions. The remaining amount of lead, approximately 13% to 26%, is weakly absorbed by carbonates and can be easily released by ion-exchangeable processes, for example.

In fly ash from the bubbling bed boiler, lead is much more liable to leach when considering the first two phases combined—that is, an acid-soluble exchangeable phase, as well as a reducible phase associated with Fe/Mn amorphous oxides. In the first sample, BFB 1, almost 33% of lead is easily releasable, and an additional 10.35% can be leached out when the soil conditions change from oxic to anoxic, while in sample BFB2 the proportions are the opposite and lead is bound in 27% of the reducible phase and only approximately 8% is easily releasable when the pH of the soil or other medium drops. Only 31% to 35% of lead is safely fixed within the mineral residuum fraction, and the remaining 22% to 34% is bound to organic matter and sulfides (as depicted in Figure 2).



A total of 26.8% to 49% of Zn in both types of fly ash should be regarded as not mobile and not available to plants, since it is safely bound with the mineralogical fraction of the ash residuum (Figure 3). However, the remaining amount of Zn, being an essential micronutrient, is potentially available under either acid-soluble, reducible, or oxidizable conditions. In both the CFB fly ash, zinc is predominantly bound with the residual phase. The content of this element in the carbonates and exchangeable fraction as well as the oxidizable fraction differs greatly within individual samples, and it ranges from 5.31% Zn in the exchangeable fraction in CFB1 to 23.45% in the second sample of the CFB ash, as well as 34.44% Zn in the oxidizable fraction of CFB1 when compared to only 14% in the CFB2 ash. In the reducible fraction associated with Fe/Mn oxides, the content of Zn is, however, comparable, and it ranges from 13.43% to 18.66%. In both the BFB ash samples, the concentrations of Zn in certain fractions are comparable. A total of 26–27% of Zn is bound with the residuum, 32–35% is associated with organic matter and sulfites, 27–31.6% of Zn is associated with the Fe/Mn oxyhydroxides, and only 9–10% of Zn is easily soluble and bioavailable from both BFB ash.

### 3.5. Acute Toxicity of Fly Ash Amendments to Plants Germination and Growth

The results of the acute toxicity test are summarized in Tables 4 and 5 and are depicted in Figure 4.

Conducting research on the potential toxic influence of biomass fly ash amendment on plants revealed no inhibition of the seed germination of *Lepidium sativum* in soil with the addition of both CFB fly ash and BFB2, whereas the inhibition of *Avena sativa* seeds from 3.3% to 6.7% was found in all mixtures of control OECD soil and the addition of fly ash, except for the CFB2 addition, where 10 out of 10 seeds of both plants germinated.

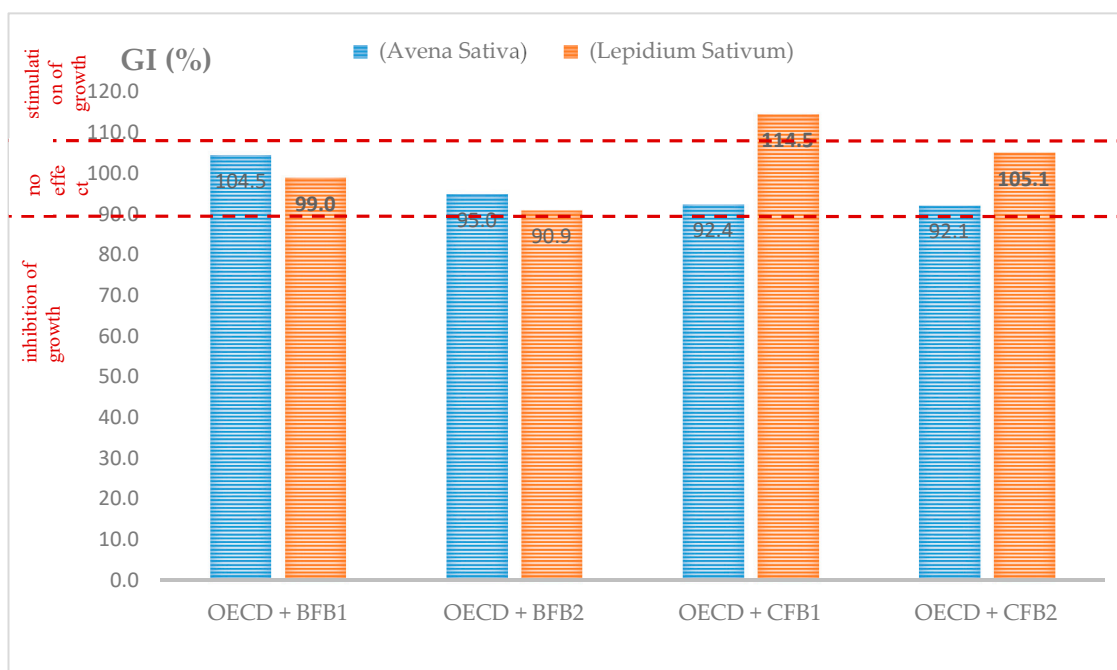
**Table 4.** Percentage inhibition of the seed germination, IG, calculated based on the average number of germinated seeds.

Mixtures	An Average Number of Germinated Seeds		The Percentage Inhibition of Seed Germination IG (%)	
	<i>Avena sativa</i>	<i>Lepidium sativum</i>	<i>Avena sativa</i>	<i>Lepidium sativum</i>
OECD control soil	10.00	10.00	-	-
OECD + BFB1	9.67	9.67	3.30	3.30
OECD + BFB2	9.67	10.00	3.30	0.00
OECD + CFB1	9.33	10.00	6.70	0.00
OECD + CFB2	10.00	10.00	0.00	0.00

**Table 5.** An average root length of the germinated seeds.

Mixtures	An Average Root Length of Germinated Seeds (mm)		Root Growth Inhibition (%)	
	<i>Avena sativa</i>	<i>Lepidium sativum</i>	<i>Avena sativa</i>	<i>Lepidium sativum</i>
OECD control soil	95.0	55.0	-	-
OECD + BFB1	102.7	56.3	-8.10 * (8.10% stimulation)	-2.36 (2.36% stimulation)
OECD + BFB2	93.3	50.0	1.79	9.09
OECD + CFB1	94.1	63.0	0.95	-14.55 (14.55% stimulation)
OECD + CFB2	87.5	57.8	7.89	-5.09 (5.09% stimulation)

\* Negative inhibition stands for stimulation (according to IO ISO Standard 11269-1: 2012 [57]).



**Figure 4.** Germination indices for *Avena sativa* and *Lepidium sativum*.

The stimulation of *Lepidium sativum* root growth was found as a result of fertilizing the soil with all ash amendments except for BFB2, whose addition caused 9% root inhibition. The best growth stimulating agent was ash from the circulating bed boiler (CRB1), which caused a 14.55% stimulation of root growth. When analyzing the *Avena sativa* root growth elongation, the results were exactly the opposite, and stimulation was found only in one sample (amended with BFB1 ash), whereas in the remaining samples the inhibition of root growth appeared in 0.95% to 7.89%. It can therefore be safely concluded that the amendment of soil with ash from the bubbling bed boiler installation was the most suitable fertilizing amendment, because it did not cause any inhibition of growth for both plants and resulted in a slight stimulation of root growth elongation (2.36% to 8.1%), depending on the plant species.

Furthermore, the Germination Index (GI), which is considered to be the most important parameter indicating the possible toxic effect of any substrate on plant growth, was calculated based on the number of germinated seeds and the root length of germinated seeds. The results depicted in Figure 4 clearly show that none of the biomass fly ash additive had any negative effect on the germination and growth of *Avena sativa* as well as *Lepidium sativum*. For both plants, the calculated GI germination rate ranged from 90.9% to 114.5%. For one sample containing an addition of fly ash from the CFB installation, the germination index indicated even a stimulation of the *Lepidium sativum* growth.

#### 4. Conclusions

Based on the results of this study, it can be concluded that the biomass fly ash obtained from the bubbling fluidized bed boilers was richer in potassium, phosphorus, carbonates, and micronutrients than the ash delivered from the circulating fluidized bed boilers. The BFB ash also contained cumulatively less contaminants such as V, Cr, Ni, As, Cd, Sb, Tl, Pb, and Hg than that from the CFB. However, when comparing the results of the Cd content with the threshold values established for liming agents (fertilizing lime and fertilizing lime containing magnesium), it becomes evident that only the fly ash from circulating fluidized bed (CFB) installation can legally be used as a direct soil liming amendment, since the Cd content of ash from the bubbling bed boilers (8.14–8.15) exceeds both the maximum acceptable concentrations of 8 mg of Cd per 1 kg of CaO as well as 5 mg of Cd per 1 kg of CaO + MgO. The difference in concentration between both types of fly ash can be attributed

to the different feedstock mixture ratio used in both plants. In the BFB boilers, a higher ratio of “agro” biomass was incinerated on top of the 79% forest biomass, including 3% straw pellets and 17% sunflower husks, whereas, in the case of CFB, 80% forest biomass as well as 20% sunflower husks were incinerated. Moreover, the BCR speciation study revealed that fly ash from both installations met the threshold values and minimum requirements set for mineral fertilizers, with the exception of the nitrogen content, which was found to be below 2 wt% in each sample. The phosphorus in all fly ash samples was, however, very poorly extractable and not easily bioavailable to plants. Active phosphorus in the form of phosphate anions was leached in negligible amounts from both the BFB as well as CFB ash, and the content of bioavailable phosphorus  $P_2O_5$  (soluble in weak acids) ranged from 20–22 mg/kg. On the other hand, the leaching test results revealed the very high mobility and bioavailability of other macronutrients, such as potassium (from 23,030 to 38,840 mg/kg), calcium (from 4410 to 6940 mg/kg), and sulfur in terms of sulfates (from 18,200 to 27,720 mg/kg). The contaminants in ash (Pb, Cd, Ce, V, Ni, As, Tl) were not easily mobile in the biomass ash, since their concentrations in aqueous leachates were negligible. A speciation BCR study revealed that almost 50% of Cd is highly mobile and bioavailable in BFB ash, since it is associated with exchangeable fractions and carbonates. Additionally, 33% to 36% of Cd is also potentially bioavailable under reducible conditions (bound with Fe/Mn oxides). Only 4–6.8% of Cd is safely bound with the residuum. In the CFB ash, approximately 50% of the Cd is available (bound with carbonates as well as Fe/Mn oxides), and can easily be remobilized under lower pH or redox conditions. Only approximately 20% of Cd is fixed in the residual fraction. The prevailing amounts of Pb (58–66%) in both samples of CFB fly ash are not bioavailable, since they are bound in the residual fraction. A total of 10% to 17% of this element is associated with organic matter and sulfides, thus indicating that lead can still be potentially released under oxidizing conditions. Zinc, a valuable micronutrient, is more bioavailable in the CFB ash than in the BFB biomass ash.

The results of an acute toxicity test also confirm that biomass fly ash amendment to soil does not have any toxic influence on plant germination and growth, despite a very high concentration of chloride anions, which are potentially detrimental to plants when appearing in such concentrations as found in both types of ash. Considering the favorable physico-chemical properties of biomass ash, especially pertaining to its high content of CaO, potassium, and other macronutrients, it is justifiable to further investigate the possible utilization approach of this particular waste (e.g., as an additive to fertilizers or as a soil improving agent), especially since this utilization approach will fit well into the waste management hierarchy as well as the circular economy policy currently promoted by EU countries. Moreover, upcoming new fertilizer regulations, which promote the idea of using organic, bio-waste, or recycled fertilizers such as biomass ash in top soils, serve to make it more justifiable to perform further research on this specific utilization approach. This is even more true when one additionally considers using this material for reclamation purposes or as a forest fertilizer. The current landfilling of biomass ash should be regarded as a highly unfavorable solution and quite simply wasteful. It, by extension, means that the entire effort put into producing energy from ecological sources was simply wasteful as well, particularly considering that this type of biomass ash, when properly treated, can easily return to the soil, thus closing the natural biogeochemical cycle.

**Author Contributions:** Conceptualization, E.J.-K.; analysis, E.J.-K. and J.P.; resources, J.P. and E.J.-K.; writing—original draft preparation, E.J.-K.; writing—review and editing, E.J.-K.; visualization (figure and table preparation), supervision, E.J.-K.; funding acquisition, E.J.-K.; data curation, E.J.-K. All authors have read and agreed to the published version of the manuscript.

**Funding:** The work was supported by the National Centre for Research and Development (NCBR) as research project no. PBS3/A2/21/2015. Publication fee was funded by the Polish National Agency for Academic Exchange under the International Academic Partnerships Programme from the project “Organization of the 9th International Scientific and Technical Conference entitled Environmental Engineering, Photogrammetry, Geoinformatics—Modern Technologies and Development Perspectives” 17–20 September 2019, Lublin, Poland.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study, in the collection, analysis, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

## References

1. Dz.U. 2014 poz. 1923. Regulation of the Minister of the Environment of 9 December 2014 on the Waste Catalog; Journal of Laws of the Republic of Poland; Journal of Laws: Warsaw, Poland, 2014.
2. Pallarès, D.; Johnsson, F. Macroscopic modelling of fluid dynamics in large-scale circulating fluidized beds. *Prog. Energy Combust. Sci.* **2006**, *32*, 539–569. [\[CrossRef\]](#)
3. Leski, K.; Luty, P.; Łucki, A.; Jankowski, D. Application of circulating fluidized bed boilers in the fuel combustion process. *Tech. Trans.* **2018**, *4*, 83–96.
4. Wang, H.; Bolan, N.; Hedley, M.; Horne, D. Potential Uses of Fluidised Bed Boiler Ash (FBA) as a Liming Material, Soil Conditioner and Sulfur Fertilizer. In *Coal Combustion Byproducts and Environmental Issues*; Sajwan, K.S., Twardowska, I., Punshon, T., Alva, A.K., Eds.; Springer: New York, NY, USA, 2006. [\[CrossRef\]](#)
5. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the chemical composition of biomass. *Fuel* **2010**, *89*, 913–933. [\[CrossRef\]](#)
6. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the composition and application of biomass ash. Part 1. Phase—mineral and chemical composition and classification. *Fuel* **2013**, *105*, 40–76. [\[CrossRef\]](#)
7. Zając, G.; Szyszlak-Bargłowicz, J.; Gołębiowski, W.; Szczepanik, M. Chemical characteristics of biomass ashes. *Energies* **2018**, *11*, 2885. [\[CrossRef\]](#)
8. Ciesielczuk, T.; Rosik-Dulewska, C.; Kochanowska, K. The Influence of biomass ash on the migration of heavy metals in the flooded soil profile—Model experiment. *Arch. Environ. Prot.* **2014**, *40*, 3–15. [\[CrossRef\]](#)
9. Ciesielczuk, T.; Kusza, G.; Nemš, A. Nawożenie popiołami z termicznego przekształcania biomasy źródłem pierwiastków śladowych dla gleb. *Ochr. Środowiska Zasobów Nat.* **2011**, *49*, 219–227. (In Polish)
10. Uliasz-Bocheńczyk, A.; Pawluk, A.; Pyzalski, M. Charakterystyka popiołów ze spalania biomasy w kotłach fluidalnych. *Miner. Resour. Manag.* **2016**, *32*, 149–162. [\[CrossRef\]](#)
11. Uliasz-Bocheńczyk, A.; Mokrzycki, E. The elemental composition of biomass ashes as a preliminary assessment of the recovery potential. *Miner. Resour. Manag.* **2018**, *34*, 115–132. [\[CrossRef\]](#)
12. Wilczyńska-Michalik, W.; Gasek, R.; Michalik, M.; Dańko, J.; Plaskota, T. Mineralogy, chemical composition and leachability of ash from biomass combustion and biomass–coal co-combustion. *Mineralogia* **2018**, *49*, 67–97. [\[CrossRef\]](#)
13. Żelazny, S.E.; Jarosiński, A. The evaluation of fertilizer obtained from fly ash derived from biomass. *Miner. Resour. Manag.* **2019**, *35*, 139–152.
14. Olanders, B.; Steenari, B.-M. Characterization of ashes from wood and straw. *Biomass Bioenergy* **1994**, *8*, 105–115. [\[CrossRef\]](#)
15. Schiemenz, K.; Eichler-Löbermann, B. Biomass ashes and their phosphorus fertilizing effect on different crops. *Nutr. Cycl. Agroecosyst.* **2010**, *87*, 471–482. [\[CrossRef\]](#)
16. Patterson, S.J.; Acharya, S.; Thomas, J.; Bertschi, A.B.; Rothwell, R.L. Integrated soil and crop management: Barley biomass and grain yield and canola seed yield response to land application of wood ash. *Agron. J.* **2004**, *96*, 971–977. [\[CrossRef\]](#)
17. Mercl, F.; Tejnecký, V.; Száková, J.; Tlustos, P. Nutrient Dynamics in Soil Solution and Wheat Response after Biomass Ash Amendments. *Agron. J.* **2016**, *108*, 2222–2234. [\[CrossRef\]](#)
18. Nabeela, F.; Murad, W.; Khan, I.; Mian, I.A.; Rehman, H.; Adnan, M.; Azizullah, A. Effect of wood ash application on the morphological, physiological and biochemical parameters of *Brassica napus* L. *Plant Physiol. Biochem.* **2015**, *95*, 15–25. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Ozolinčius, R.; Varnagirytė, I.; Armolaitis, K.; Karlton, E. Initial effects of wood ash fertilization on soil, needle and litterfall chemistry in a Scots Pine (*Pinus sylvestris* L). *stand. Balt. For.* **2005**, *11*, 21.
20. Nurmesniemi, H.; Mänskinen, K.; Poykio, R.; Dahl, O. Forest fertilizer properties of the bottom ash and fly ash from a large-sized (115 MW) industrial power plant incinerating wood-based biomass residues. *J. Univ. Chem. Technol. Met.* **2012**, *47*, 43–52.
21. Ohenoja, K.; Pesonen, J.; Yliniemi, J.; Illikainen, M. Utilization of Fly Ashes from Fluidized Bed Combustion: A Review. *Sustainability* **2020**, *12*, 2988. [\[CrossRef\]](#)

22. Phongpan, S.; Mosier, A. Impact of organic residue management on nitrogen use efficiency in an annual rice cropping sequence of lowland Central Thailand. *Nutr. Cycl. Agroecosyst.* **2003**, *66*, 233–240. [CrossRef]
23. Ikpe, F.N.; Powell, J.M. Nutrient cycling practices and changes in soil properties in the crop-livestock farming systems of western Niger Republic of West Africa. *Nutr. Cycl. Agroecosyst.* **2002**, *62*, 37–45. [CrossRef]
24. Saletnik, B.; Bajcar, M.; Zagula, G.; Czernick, M.; Puchalski, C. Influence of biochar and biomass ash applied as soil amendment on germination rate of Virginia mallow seeds (*Sida hermaphrodita* R.). *Econtechmod. An Int. Q. J.* **2016**, *5*, 71–76.
25. Owolabi, O.; Ojeniyi, S.; Amodu, A.; Hazzan, K. Response of cowpea, okra and tomato sawdust ash manure. *Moor J. Agric. Res.* **2003**, *4*, 178–182. [CrossRef]
26. Meller, E.; Bilenda, E. Wpływ popiołów ze spalania biomasy na właściwości fizykochemiczne gleb lekkich. *Polityka Energetyczna* **2012**, *15*, 287–292. (In Polish)
27. Ayeni, L.S.; Oso, O.P.; Ojeniyi, S.O. Effect of sawdust and wood ash application in improving soil chemical properties and growth of cocoa (*Theobroma cacao*) seedlings in the Nurseries. *Agric. J.* **2008**, *3*, 323–326.
28. Dahl, O.; Nurmesniemi, H.; Poykio, R.; Watkins, G. Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. *Fuel Process. Technol.* **2010**, *91*, 1634–1639. [CrossRef]
29. Ohenoja, K.; Tanskanen, P.; Wigren, V.; Kinnunen, P.; Körkkö, M.; Peltosaari, O.; Österbacka, J.; Illikainen, M. Self-hardening of fly ashes from a bubbling fluidized bed combustion of peat, forest industry residuals, and wastes. *Fuel* **2016**, *165*, 440–446. [CrossRef]
30. Dahl, O.; Nurmesniemi, H.; Pöykio, R.; Watkins, G. Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler. *Fuel Process. Technol.* **2009**, *90*, 871–878. [CrossRef]
31. Nurmesniemi, H.; Mäkelä, M.; Poykio, R.; Manskinen, K.; Dahl, O. Comparison of the forest fertilizer properties of ash fractions from two power plants of pulp and paper mills incinerating biomass-based fuels. *Fuel Process. Technol.* **2012**, *104*, 1–6. [CrossRef]
32. Pöykio, R.; Nurmesniemi, H.; Keiski, R.L. Total and size fractionated concentrations of metals in combustion ash from forest residues and peat. *Proc. Est. Acad. Sci.* **2009**, *58*, 247–255. [CrossRef]
33. Pöykio, R.; Nurmesniemi, H.; Perämäki, P.; Kuokkanen, T.; Välimäki, I. Leachability of metals in fly ash from a pulp and paper mill complex and environmental risk characterization for eco-efficient utilization of the fly ash as a fertilizer. *Chem. Speciat. Bioavailab.* **2005**, *17*, 1–9. [CrossRef]
34. FINLEX®-Viranomaisten Määräyskokoelmat: Maa- ja Metsätalousministeriö-01.09.2011 1784/14/2011. n.d. Available online: <http://www.finlex.fi/fi/viranomaiset/normi/400001/37638> (accessed on 1 September 2020).
35. Bekendtgørelse om Anvendelse af Bioaske til Jordbrugsformål (Bioaskebekendtgørelsen)-Retsinformation.dk. n.d. Available online: <https://www.retsinformation.dk/forms/r0710.aspx?id=116609> (accessed on 1 September 2020).
36. Van Dijen, F. Bioefficiency. Ash Utilization-Draft for Technical Regulations (D6.3). Ref.Ares(2019)645078518/10/2019. Available online: <https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5c82e4e2f&appId=PPGMS> (accessed on 1 September 2020).
37. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 Laying down Rules on the Making Available on the Market of EU Fertilising Products and Amending Regulations (EC) No. 1069/2009 and (EC) No. 1107/2009 and repealing Regulation (EC) No 2003/2003. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32019R1009> (accessed on 1 September 2020).
38. Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of 13 October 2003 Relating to Fertilisers. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32003R2003&from=EN> (accessed on 1 September 2020).
39. European Committee for Standardization. EN 196-2:2013. *Method of Testing Cement. Chemical Analysis of Cement*; European Committee for Standardization (CEN) Standards: Brussels, Belgium, 2013.
40. Polish Committee for Standardization. *Standard PN EN 13657: 2006, Characterization of Waste-Digestion for Subsequent Determination of Aqua Regia Soluble Portion of Elements*; Polish Committee for Standardization: Warsaw, Poland, 2006.
41. Polish Committee for Standardization. *Standard PN EN ISO 17294-2: 2016-11, Water Quality-Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS)-Part 2: Determination of selected elements including Uranium Isotopes (ISO 17294-2:2016)*; Polish Committee for Standardization: Warsaw, Poland, 2006.



42. Polish Committee for Standardization. *Standard PN-EN 15407:2011, Solid Recovered Fuels-Methods for the Determination of Carbon (C), Hydrogen (H) and Nitrogen (N) Content*; Polish Committee for Standardization: Warsaw, Poland, 2011.
43. Polish Committee for Standardization. *Standard PN-EN 15408:2011, Solid Recovered Fuels-Methods for the Determination of Sulphur (S), Chlorine (Cl), Fluorine (F) and Bromine (Br) content*; Polish Committee for Standardization: Warsaw, Poland, 2011.
44. Polish Committee for Standardization. *Standard PN-EN 12457:2006. Characterisation of Waste. Leaching. Compliance Test for Leaching of Granular Waste Materials and Sludges. Part 1–4*; Polish Committee for Standardization: Warsaw, Poland, 2006.
45. Polish Committee for Standardization. *Standard EN ISO 10304-1:2009/AC:2012 Water Quality—Determination of Dissolved Anions by Liquid Chromatography of Ions—Part 1: Determination of Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate and Sulfate—Technical Corrigendum 1 (ISO 10304-1:2007/Cor 1:2010)*; Polish Committee for Standardization: Warsaw, Poland, 2012.
46. Polish Committee for Standardization. *Standard PN EN ISO 14911:2002. Water Quality-Determination of Dissolved L[I+], N[A+], NH[4 +], K[+], MN[2+], CA[2+], MG[2+], SR[2+] AND BA[2+] Using Ion Chromatography-Method for Water and Waste Water*; Polish Committee for Standardization: Warsaw, Poland, 2002.
47. Polish Committee for Standardization. *Standard PN-R-04023:1996. Chemical and Agricultural Analysis of soil—Determination of Available Phosphorus Content in Mineral Soils*; Polish Committee for Standardization: Warsaw, Poland, 1996.
48. Polish Committee for Standardization. *Standard PN-R-04023:1996/A1:2002. Chemical and Agricultural Analysis of Soil—Determination of Available Potassium in Mineral Soils*; Polish Committee for Standardization: Warsaw, Poland, 2002.
49. Tessier, A.; Campbell, P.G.C.; Bisson, M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **1979**, *51*, 844–851. [\[CrossRef\]](#)
50. Ure, A.M.; Quevauviller, P.; Muntau, H.; Griepink, B. Speciation of Heavy Metals in Soils and Sediments. An Account of the Improvement and Harmonization of Extraction Techniques Undertaken Under the Auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 135–151. [\[CrossRef\]](#)
51. Polish Committee for Standardization. *Standard PN EN ISO 17294-1: 2007-11, Water Quality—Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS)-Part 1: General guidelines*; Polish Committee for Standardization: Warsaw, Poland, 2007.
52. Gariglio, N.F.; Buyatti, M.A.; Pilatti, R.A.; Russia, D.E.G.; Acosta, M.R. Use of a germination bioassay to test compost maturity of willow (*Salix* sp.) sawdust. *N. Z. J. Crop. Hortic. Sci.* **2002**, *30*, 135–139. [\[CrossRef\]](#)
53. Ciesielczuk, T.; Rosik-Dulewska, C.; Poluszyńska, J.; Miłek, D.; Szewczyk, A.; Sławińska, I. Acute Toxicity of Experimental Fertilizers Made of Spent Coffee Grounds. *Waste Biomass Valorization* **2017**, *9*, 2157–2164. [\[CrossRef\]](#)
54. Teacă, C.A.; Bodîrlău, R. Assessment of toxicity of industrial waste crop plant assays. *BioResources* **2008**, *3*, 1130–1145.
55. Oleszczuk, P.; Hollert, H. Comparison of sewage sludge toxicity to plants and invertebrates in three different soils. *Chemosphere* **2011**, *83*, 502–509. [\[CrossRef\]](#)
56. Baran, A.; Tarnawski, M. Phytotoxkit/Phytotestkit and Microtox® as tools for toxicity assessment of sediments. *Ecotoxicol. Environ. Saf.* **2013**, *98*, 19–27. [\[CrossRef\]](#)
57. Polish Committee for Standardization. *Standard PN EN ISO 11269-1: 2013, Soil Quality—Determination of the Effects of Pollutants on Soil Flora—Part 1: Method for Measurement of Inhibition of Root Growth (ISO 11269-1:2012)*; Polish Committee for Standardization: Warsaw, Poland, 2013.
58. Uliasz-Bocheńczyk, A.; Pawluk, A.; Sierka, J. Wymywalności zanieczyszczeń z popiołów lotnych ze spalania biomasy. *Miner. Resour. Manag.* **2015**, *31*, 145–156.
59. Dz.U. 119.765. *Regulation of the Minister of Agriculture and Rural Development of June 18, 2008 on the Implementation of Certain Provisions of the Act on Fertilizers and Fertilization*; Journal of Laws of the Republic of Poland: Warsaw, Poland, 2008.
60. Saletnik, B.; Zaguła, G.; Bajcar, M.; Czernicka, M.; Puchalski, C. Biochar and biomass ash as a soil ameliorant: The effect on selected soil properties and yield of Giant Miscanthus (*Miscanthus × giganteus*). *Energies* **2018**, *11*, 2535. [\[CrossRef\]](#)



61. Zapałowska, A.; Puchalski, C.; Hury, G.; Makarewicz, A. Influence of fertilization with the use of biomass ash and sewage sludge on the chemical composition of Jerusalem Artichoke used for energy related purposes. *J. Ecol. Eng.* **2017**, *18*, 235–245. [\[CrossRef\]](#)
62. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G.; Morgan, T.J. An overview of the organic and inorganic phase composition of biomass. *Fuel* **2012**, *94*, 1–33. [\[CrossRef\]](#)
63. Cobreros, C.; Reyes-Araiza, J.L.; Manzano-Ramírez, A.; Nava, R.; Rodríguez, M.; Mondragón-Figueroa, M.; Apátiga, L.M.; Rivera-Muñoz, E.M. Barley straw ash: Pozzolanic activity and comparison with other natural and artificial pozzolans from Mexico. *BioResources* **2015**, *10*, 3757–3774. [\[CrossRef\]](#)
64. Jaworek, A.; Czech, T.; Sobczyk, A.T.; Krupa, A. Properties of biomass vs. coal fly ashes deposited in electrostatic precipitator. *J. Electrostat.* **2013**, *71*, 165–175. [\[CrossRef\]](#)
65. García-Jiménez, A.; Trejo-Téllez, L.I.; Guillén-Sánchez, D.; Gómez-Merino, F.C. Vanadium stimulates pepper plant growth and flowering, increases concentrations of amino acids, sugars and chlorophylls, and modifies nutrient concentrations. *PLoS ONE* **2018**, *13*, e0201908. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Wang, J.F.; Liu, Z. Effect of vanadium on the growth of soybean seedlings. *Plant Soil* **1999**, *216*, 47–51. [\[CrossRef\]](#)
67. Shanker, A.; Djanaguiraman, M.; Venkateswarlu, B. Chromium interactions in plants: Current status and future strategies. *Metallomics* **2009**, *1*, 375–383. [\[CrossRef\]](#)
68. Dz.U. 2016 poz. 1395. *Regulation of the Minister of the Environment of September 1, 2016 on the Method of Assessing the Pollution of the Earth's Surface*; Journal of Laws of the Republic of Poland: Warsaw, Poland, 2016.
69. Badura, L. Metale w glebach stan zagrożenia na przykładzie województwa katowickiego. In *Ekologiczne problemy Górnego Śląska*, red J. Śliwiok. Wyd; Wszechnica Górnośląskiego Towarzystwa Przyjaciół Nauk im. W. Roździeńskiego: Katowice, Poland, 1995. (In Polish)
70. Wang, L.K.; Chen, J.P.; Hung, Y.; Shammis, N.K. *Heavy Metals in the Environment*; CRP Press Taylor & Francis Group: Boca Raton, FL, USA, 2009.
71. Abbasi, S.A.; Abbasi, N.; Soni, R. *Heavy Metals in the Environment*; Mittal Publications: New Delhi, India, 2019.
72. Bååth, E. Effects of heavy metals in soil on microbial processes and populations (a review). *Water Air Soil Pollut.* **1989**, *47*, 335–379. [\[CrossRef\]](#)
73. Zhao, F.-J.; Tausz, M.; De Kok, L.J. Role of Sulfur for Plant Production in Agricultural and Natural Ecosystems. In *Sulfur Metabolism in Phototrophic Organisms*; Hell, R., Dahl, C., Knaff, D., Leustek, T., Eds.; Springer: Dordrecht, The Netherlands, 2008; Volume 27, pp. 417–435.
74. Hawkesford, M.J. Plant responses to sulphur deficiency and the genetic manipulation of sulphate transporters to improve S-utilization efficiency. *J. Exp. Bot.* **2000**, *51*, 131–138. [\[CrossRef\]](#)
75. Tavakkoli, E.; Rengasamy, P.; McDonald, G.K. High concentrations of Na<sup>+</sup> and Cl<sup>−</sup> ions in soil solution have simultaneous detrimental effects on growth of faba bean under salinity stress. *J. Exp. Bot.* **2010**, *61*, 4449–4459. [\[CrossRef\]](#)
76. Ohno, T. Effect of wood ash application on soil pH and soil test nutrient levels. *Agric. Ecosyst. Environ.* **1990**, *32*, 223–239. [\[CrossRef\]](#)
77. Pels, J.R.; De Nie, D.S.; Kiel, J.H.A. Utilization of ashes from biomass combustion and gasification. In *Proceedings of the 14th European Biomass Conference & Exhibition, Paris, France, 17–21 October 2005*. ECN-RX-05-182.
78. Sarkar, S.K.; Favas, P.J.C.; Rakshit, D.; Satpathy, K.K. Geochemical speciation and risk assessment of heavy metals in soils and sediments. In *Environmental Risk Assessment of Soil Contamination*; Hernandez-Soriano, M.C., Ed.; InTech: London, UK, 2014; p. 918.
79. Agrawal, R.; Kumar, B.; Priyanka, K.; Narayan, C.; Shukla, K.; Sarkar, J. Anshumali Micronutrient Fractionation in Coal Mine-Affected Agricultural Soils, India. *Bull. Environ. Contam. Toxicol.* **2016**, *96*, 449–457. [\[CrossRef\]](#) [\[PubMed\]](#)
80. Dong, D. Adsorption of Pb and Cd onto metal oxides and organic material in natural surface coatings as determined by selective extractions: New evidence for the importance of Mn and Fe oxides. *Water Res.* **2000**, *34*, 427–436. [\[CrossRef\]](#)

