Environmental Application of Ash from Incinerated Biomass

Jadwiga Wierzbowska*, Stanislaw Sienkiewicz, Piotr Żarczyński and Sławomir Krzebietke

Chair of Agricultural Chemistry and Environmental Protection, Faculty of Environmental Management and Agriculture, University of Warmia and Mazury, 10 719 Olsztyn, Poland; jadwiga.wierzbowska@uwm.edu.pl (J.W.); piotr.zarczynski@uwm.edu.pl (P.Z.); slawomir.krzebietke@uwm.edu.pl (S.K.)

* Correspondence: stasien@uwm.edu.pl

Received: 20 January 2020; Accepted: 30 March 2020; Published: 1 April 2020

Abstract: The purpose of this study was to evaluate the effect of ash from combustion of plant biomass of energy willow and Pennsylvania fanpetals on yields of willow grown as an energy crop and on soil properties. A three-year pot experiment was carried out on substrates with a loamy sand texture. Ash application rates were based on the potassium fertilisation demand. An incubation experiment was carried out to determine the effect of biomass-based ash on soil properties. Three soils with textural categories were incubated for 3 months with the ashes, the doses of which were determined on the basis of the hydrolytic acidity of soils (1/4; 1/2 and 1.0 Hh). It was found that ashes generated from burning willow or Pennsylvania fanpetals can be applied instead of phosphorus, potassium and magnesium fertilisers in the cultivation of energy willow. The plant uptake of P, K and Mg from the ashes did not diverge from their absorption by plants when supplied with mineral salts. The application of these alkaline ashes will increase the soil content of phytoavailable forms of phosphorus, potassium and magnesium. The examined ashes enriched the soil with micronutrients.

Keywords: ash from combustion of plant biomass; willow yield; content of macronutrients in willow biomass; selected properties of soil

1. Introduction

The constantly growing demand for energy, depleting energy resources, as well as the need to limit undesirable changes in the environment, stimulate interest in energy from renewable sources. Energy generated from biomass is gaining increasingly widespread use in commercial energy generation, especially in the geographical and climatic conditions of Poland [1]. The most popular biomass-based solid fuel originates from forest wood biomass, although fuels obtained from agricultural biomass are gaining importance as well [2,3].

As with the combustion of coal or lignite, the burning of biomass generates solid waste, mainly fly ash, and the quantity and quality of such waste depends on the type of biomass used [4–7]. According to the concept of sustainable development and in compliance with the law on renewable energy resources and broadly understood environmental protection, the most beneficial way to utilise the fly ash obtained from the incineration of plant biomass is to return the residue to the soil [5,8–12]. Ash from plant biomass can be used as a fertiliser in the cultivation of energy crops. Biochar and biomass ash, if applied in proper doses, have a beneficial effect on the chemical properties of soil, leading to increased crop yields. Biochar mixed with biomass ash is a possible alternative to traditional mineral fertilisers, and this may even enhance the ecological aspect of renewable energy use [13]. Because of its properties, ash produced from woody biomass can also be used to condition sewage sludge. Conditioned sewage sludge can provide considerable nutrients for perennial crops [14].
The chemical composition of biomass-derived ash depends on what plant materials have been used for energy generation. One of the key parameters which dictates the way ash could be used is its chemical composition. The prevalent elements in ash are Ca, K, P and S, whereas toxic elements are usually found in small concentrations, which suggests that agricultural use of ash is possible. Moreover, ash obtained from biomass can enrich soil with micronutrients, such as Zn, Cu and Mn, which is another argument in favour of using ash as a fertiliser. Whether biomass-based ash can be applied in agriculture is a question that needs to be resolved in every single case, depending on the origin of biomass [5,6,15,16]. The content of phosphorus, potassium, calcium and magnesium in bottom and fly ash obtained from burning wooden pellets and rye straw justifies the use of this material to fertilise soils [17]. Although ash can provide nutrients for plants and has deacidifying properties, it can also be a source of harmful substances (mainly heavy metals) and its form of dust makes the application more difficult [18,19]. The content of trace elements in ash from combustion of grasses (*Phragmites australis* and *Arundo donax*) harvested from areas polluted with municipal wastewater was 1.5 to 3-fold higher than in plant tissues. However, even these amounts were much lower than the allowed quantities of heavy metals in substances used in agriculture and forestry [10].

The purpose of this study has been to evaluate the effect of ash from the combustion of plant biomass on yields of willow grown as an energy crop and on soil properties.

2. Materials and Methods

2.1. A Plant Growing Experiment

A three-year experiment, with four replications, was carried out in Kick-Brauckman pots each filled with 10 kg of substrate of the texture representing loamy sand. Three willow plants were grown in each pot. Before the experiment began, the pH of soil in 1 mol KCl dm\(^{-3}\) was 5.70. The content of available forms of macronutrients was as follows: P—86.0, K—193.0 and Mg—72.6 mg kg\(^{-1}\) of soil. The soil also contained 8.90 g kg\(^{-1}\) C-organic and 0.91 g kg\(^{-1}\) N-total. The ash used for the fertilisation of willow plants originated from the combustion of biomass of energy willow and Pennsylvania fanpetals (Table 1).

| Alkalinity % CaO | P         | K         | Mg         | Ca         | Cu         | Zn         | Mn         | Fe         | Ni         | Cd * | Pb * | Cr |
|------------------|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|------|------|----|
| Ash from energy willow | 21.40 ± 0.61 | 33.06 ± 0.81 | 65.97 ± 1.82 | 12.43 ± 0.60 | 226.56 ± 2.85 | 0.73 ± 0.02 | 1.65 ± 0.03 | 1.67 ± 0.05 | 7.70 ± 0.50 | 0.21 ± 0.02 | 0.05 ± 0.01 | 2.84 ± 0.06 | 0.60 ± 0.03 |
| Ash from Pennsylvania fanpetals | 37.80 ± 1.55 | 16.67 ± 1.02 | 43.37 ± 1.39 | 10.68 ± 0.66 | 305.76 ± 17.58 | 0.67 ± 0.04 | 2.42 ± 0.02 | 1.33 ± 0.02 | 1.51 ± 0.01 | 0.21 ± 0.02 | 0.07 ± 0.02 | 3.06 ± 0.08 | 0.51 ± 0.04 |

* allowable content of Cd and Pb in mineral fertilizers is 50 and 140 mg kg\(^{-1}\), respectively [20].

The doses of ash were based on the potassium fertilisation demand (Table 2). To evaluate the fertilisation effect of ash, variants fertilised solely with mineral components (KH\(_2\)PO\(_4\), KCl and Mg(NO\(_3\))\(_2\)·H\(_2\)O) were set up. All fertilisation variants (except the control) were added a dose of 0.5 g N per pot in the form of NH\(_4\)NO\(_3\). All fertilising components and ash were added to soil prior to planting willow. Every year, willow was grown from unrooted cuttings of willow shoots. Willow shoots were harvested in autumn, after the end of the plant growing season (leaf shedding).

2.2. Laboratory Experiment

An incubation experiment was carried out to determine the effect of biomass-based ash on soil properties. The textural composition of soil was determined using a laser grain-size meter Mastersizer 2000PB 33 ed. 2 03.12.2012. The selected properties of soil before the experiment are presented in Table 3. In comparison with the ash from Pennsylvania fanpetals, the ash from energy willow contained...
twice as much phosphorus and 5 times as much iron. It was also much richer in K and had slightly more Mg than the ash from Pennsylvania fanpetals. In turn, the ash from Pennsylvania fanpetals contained much more calcium. The content of Cu, Ni, Cd and Cr of both ashes was similar. The content of Cd and Pb in the ashes was below the permissible amounts of these elements in mineral fertilisers.

Table 2. The design of the plant trials.

| Specification | K  | P  | Mg | Ca  |
|---------------|----|----|----|-----|
| Control       |    |    |    |     |
| Only N        |    |    |    |     |
| Ash from energy willow (AEW) |    |    |    |     |
| D I ash + N   | 0.30 | 0.16 | 0.06 | 1.15 |
| NPKMgCa       | 0.30 | 0.16 | 0.06 | 1.15 |
| D II ash + N  | 0.60 | 0.33 | 0.11 | 2.31 |
| NPKMgCa       | 0.60 | 0.33 | 0.11 | 2.31 |
| D III ash + N | 0.90 | 0.50 | 0.17 | 3.46 |
| NPKMgCa       | 0.90 | 0.50 | 0.17 | 3.46 |
| Ash from Pennsylvania fanpetals (APF) |    |    |    |     |
| D I ash + N   | 0.30 | 0.14 | 0.07 | 2.60 |
| NPKMgCa       | 0.30 | 0.14 | 0.07 | 2.60 |
| D II ash + N  | 0.60 | 0.28 | 0.15 | 5.20 |
| NPKMgCa       | 0.60 | 0.28 | 0.15 | 5.20 |
| D III ash + N | 0.90 | 0.42 | 0.22 | 7.79 |
| NPKMgCa       | 0.90 | 0.42 | 0.22 | 7.79 |

Table 3. Selected properties of the soil prior to the experiment.

| Agronomic Category of Soil * | Textural Classes * | pH H2O 1 mol dm3 KCl | pH Hh [mmol(+)/kg⁻¹] |
|------------------------------|--------------------|----------------------|---------------------|
| Very light                   | sand               | 5.90                 | 5.58                | 22.5               |
|                              | clay fraction (<0.002 mm)–0.4% |                     |                     |                    |
|                              | silt fraction (0.002–0.05 mm)–10.6% |                     |                     |                    |
|                              | sand fraction (0.05–2.0 mm)–89.0% |                     |                     |                    |
| Light                        | loamy sand         | 6.12                 | 5.86                | 22.8               |
|                              | clay fraction (<0.002 mm)–1.6% |                     |                     |                    |
|                              | silt fraction (0.002–0.05 mm)–19.5% |                     |                     |                    |
|                              | sand fraction (0.05–2.0 mm)–78.9% |                     |                     |                    |
| Medium                       | sandy loam         | 5.85                 | 5.14                | 28.1               |
|                              | clay fraction (<0.002 mm)–3.9% |                     |                     |                    |
|                              | silt fraction (0.002–0.05 mm)–36.8% |                     |                     |                    |
|                              | sand fraction (0.05–2.0 mm)–59.3% |                     |                     |                    |

* Particle size [20].

Soils with different textural categories were sampled from the depth of 0–25 cm, dried and sifted through a sieve with a 2 mm mesh size. Next, portions of 200 g of each soil were put in glass vessels together with appropriate amounts of ash (Table 3). Doses of ash were determined based on the alkalinity and hydrolytic acidity of the analysed soils (0.25; 0.50 and 1.0 Hh). Throughout the incubation period, the soil moisture content was maintained at 60% of full water capacity. Soil and ash mixtures were incubated for 3 months at a temperature 20 °C.

2.3. Methods of Chemical Analyses of Soils and Plants

The plant material was wet mineralised in concentrated sulphuric acid (H2SO4) with added hydrogen peroxide (H2O2) as the oxidant (BÜCHI Speed Digester K-439). The following determinations
were made in the mineralised plant material: content of nitrogen (N) with the Kjeldahl method (on a KjelFlex K−360 apparatus); phosphorus (P) by colorimetry with the vanadate-molybdate method (Shimadzu UV 1201V); potassium (K), calcium (Ca) and sodium (Na) by atomic emission spectrometry (AES) (Jenway LTD PFP 7) and magnesium by atomic absorption spectrometry (AAS) (Shimadzu AA-6800).

After the incubation, the soil samples underwent determination of the available P and K content with the Egner–Riehm method and Mg according to the Schachtschabel method. Potassium extracted from soil with buffered calcium lactate (pH = 3.6) was determined by the flame photometric method (on a Jenway LTD PFP 7 apparatus) and phosphorus was assessed by colorimetry with the molybdate method (Shimadzu UV 1201V). Magnesium extracted with a solution of 0.0125 mol CaCl₂·6H₂O dm⁻³ was determined with the atomic absorption method (Shimadzu AA-6800). The content of trace elements extracted from soil with a solution of 1 mol HCl dm⁻³ was determined with the ASA method on a Shimadzu AA-6800 device. Finally, the hydrolytic acidity of soil after extraction with 0.5 mol (CH₃COO)₂Ca dm⁻³ was determined with the Kappen method [21,22].

Macronutrients and trace elements from the ash were extracted with concentrated sulphuric acid, and then the content of P was measured colorimetrically with the vanadate-molybdate method (Shimadzu UV 1201V); K and Ca were determined by atomic emission spectrophotometry (AES) (Jenway LTD PFP 7), whereas Mg and trace elements were assayed using the atomic absorption spectrometric method on a Shimadzu AA-6800.

The determinations were completed by referring to certified material (Trace Metals–Sewage Sludge 4, Sigma-Aldrich RTC, Inc.), Table 4.

**Table 4.** The determinations compared with the certified material (Trace Metals–Sewage Sludge 4, Sigma-Aldrich RTC, Inc.).

| Value of Determination | Cu      | Pb      | Ni      | Cr       | Zn       | Mn       | Fe       |
|------------------------|---------|---------|---------|----------|----------|----------|----------|
| Certified value [mg kg⁻¹ d.m.] | 482 ± 50.4 | 154 ± 12.4 | 163 ± 13.5 | 289 ± 30.4 | 1240 ± 181 | 693 ± 108 | 20,100 ± 4390 |
| Determination value [mg kg⁻¹ d.m.] | 455.5 | 153.2 | 160.8 | 280.9 | 1075.6 | 615.2 | 22,398 |
| Precision of determination [%] | 94.5 | 99.5 | 98.7 | 97.2 | 86.7 | 88.8 | 111.4 |

2.4. Statistical Calculations

The results were processed statistically with the help of STATISTICA 13 software package, and differences between means were compared according to Tukey’s test at a level of significance equal \( p < 0.01 \).

3. Results, Research and Discussion

The fresh matter yield of willow shoots ranged from 43.6 to 142.6 g per pot (Table 5). In comparison with plants grown without fertilisation, plants supplied only nitrogen produced three times as much fresh mass as willow shoots. Ash from energy willow and ash from Pennsylvania fanpetals caused a further, albeit insignificant, increase in the yield of fresh matter of the plants. Ash from incinerated energy willow was found to have produced a slightly better yield-stimulating effect.

The dry matter yield of willow shoots was in a range of 20.0 to 72.4 g per pot, and exclusive nitrogen fertilisation trebled the dry matter yield of shoots. Same as for fresh matter, soil enrichment with ash produced from the burning of energy crops or with equivalent amounts of nutrients in the form of salts caused a small increase in dry matter yields, which proved not to be statistically significant. The content of dry matter in willow shoots from the control variants (without fertilisation) was 47.9%, while fertilisation with nitrogen alone contributed to a significant increase (to 51.4%) in the content of dry matter in plants. The doses of ash or their type did not have any significant influence on the content of dry matter in plants.
Shoots of the willow plants fertilised only with nitrogen contained significantly more nitrogen and calcium (6.33 and 4.68 g kg\(^{-1}\) d.m., respectively) than shoots of the control plants (4.79 and 4.16 g kg\(^{-1}\) d.m., respectively) (Table 6). Likewise, the content of potassium increased under the influence of N fertilisation, but the difference was not confirmed as statistically significant. The fertilisation of soil with ash or the application of equivalent quantities of nutrients as mineral salts only slightly modified the content of nitrogen in willow shoots. Concentrations of P, K and Na in willow biomass tended to increase as the doses of both types of ash or fertilising elements in the form of mineral salts increased. The content of Ca in the willow shoots increased as the amount of ash from the Pennsylvania fanpetals added to the soil was higher. The doses of the two types of ash had no effect on the content of Mg in plants. Although no statistically significant differences were confirmed, it was possible to observe a tendency towards the greater accumulation of N, P and Na in the shoots of the willow fertilised with Pennsylvania fanpetals ash. The highest Ca content was determined in shoots of willow plants fertilised with ash from Pennsylvania fanpetals.

**Table 5.** Willow yield (average from 3 years of research).

| Specification | Fresh Matter | Dry Matter | Content of Dry Matter |
|---------------|--------------|------------|-----------------------|
|               | AEW          | AFP        | AEW                   | AFP         |
|               | g per pot    | %          | g per pot             | %           |
| Control       | 43.6 a *     | 20.0 a     | 47.9 a                |
| Only N        | 121.7 b      | 62.4 b     | 51.4 c                |
| D I ash + N   | 132.0 b      | 64.2 b     | 46.5 b                |
| NPKMgCa       | 138.0 b      | 68.4 b     | 50.1 b                |
| D II ash + N  | 139.8 b      | 71.0 b     | 50.7 b                |
| NPKMgCa       | 137.9 b      | 70.2 b     | 49.5 b                |
| D III ash + N | 138.8 b      | 69.9 b     | 50.5 b                |
| NPKMgCa       | 142.6 b      | 72.4 b     | 50.6 b                |
| Average for ash type | 136.9 A | 133.0 A | 68.4 A |
| * data marked with the same letters do not differ significantly at \(p < 0.01\); AEW—ash from energy willow; APF—ash from Pennsylvania fanpetals.

**Table 6.** Content of macronutrients in willow biomass (average from 3 years of research).

| Specification | N       | P       | K       | Ca      | Mg      | Na      |
|---------------|---------|---------|---------|---------|---------|---------|
|               | g kg\(^{-1}\) d.m. |
| Control       | 4.79 a * | 1.92 a  | 5.34 a  | 4.16 a  | 0.59 a  | 0.92 d  |
| Only N        | 6.33 b  | 1.94 a  | 5.83 a  | 4.68 b  | 0.59 a  | 0.85 b–d|
| Ash from energy willow (AEW) | 6.46 b | 2.08 a | 6.52 ab | 4.66 b | 0.56 a | 0.58 a |
| Ash from Pennsylvania fanpetals (APF) | 6.67 a | 2.08 a | 6.09 ab | 4.07 a | 0.56 a | 0.86 b–d|
| D I ash + N   | 6.42 b  | 2.08 a  | 6.34 ab | 4.36 ab | 0.54 a  | 0.63 a  |
| NPKMgCa       | 6.31 b  | 2.27 b  | 6.73 ab | 3.98 a  | 0.55 a  | 0.70 ab  |
| D II ash + N  | 6.17 b  | 2.20 ab | 6.80 ab | 4.06 a  | 0.55 a  | 0.72 a–c|
| NPKMgCa       | 6.28 b  | 2.38 b  | 7.07 b  | 4.56 b  | 0.58 a  | 0.84 b–d|
| D III ash + N | 6.52 b  | 2.27 b  | 7.25 b  | 4.47 ab | 0.62 a  | 0.97 d  |
| Average for ash type | 6.50 a | 2.06 a | 6.09 ab | 4.07 a | 0.56 a | 0.86 b–d|
| D I ash + N   | 6.67 b  | 2.08 a  | 6.07 ab | 4.02 a  | 0.56 a  | 0.88 cd |
| NPKMgCa       | 6.63 b  | 2.15 ab | 6.46 ab | 4.35 ab | 0.59 a  | 0.92 d  |
| D II ash + N  | 6.63 b  | 2.16 ab | 6.45 ab | 4.49 ab | 0.60 a  | 0.92 d  |
| NPKMgCa       | 6.70 b  | 2.26 b  | 7.03 b  | 4.61 b  | 0.61 a  | 0.95 d  |
| D III Ash + N | 6.82 b  | 2.26 b  | 7.17 b  | 4.89 b  | 0.62 a  | 1.12 e  |
| Average for ash type | 6.35 A | 2.27 A | 7.03 A | 4.49 A | 0.56 A | 0.71 A |
| * data marked with the same letters do not differ significantly at \(p < 0.01\).
Ash applications did not cause any statistically verifiable differences in the number of shoots and stocks or the height and green mass of the test plants. The increased nutrient supply of the soil through the treatments was not reflected in the nutrient content of the plants during the first year [12]. In other studies [23], ash from reed canary grass could be used as a substitute of phosphorus fertilisers in the cultivation of this plant for energy purposes. The yield-stimulating effect of reed canary grass ash is comparable to that produced by commercial phosphorus fertilisers, although the biomass of crops contained more crude ash after the application of ash. Ash from reed canary grass did not affect the content of available P and K forms in the soil, even though it raised the soil content of Ca and Mg. Another study, conducted by Li et al. [24] demonstrated that ash from biomass was characterised by the availability of phosphorus similar to that of easily soluble phosphorus fertilisers, but it limited the uptake of cadmium by plants due to its alkaline reaction.

Different doses of ash obtained from the incineration of sewage sludge did not have any influence on the content of sodium and magnesium in the aerial biomass of Pennsylvania fanpetals, but the highest dose of ash applied significantly raised the content of calcium in the plant material analysed [25]. Another experiment showed that biochar, ash from biomass or a mixture of both used for soil fertilisation significantly improved the content of potassium in aerial parts of Pennsylvania fanpetals [26].

Among the macronutrients added to soil together with ash, in the first year after the application plants most readily absorbed potassium and took up the least of magnesium (Figure 1). More K was accumulated by plants fertilised with ash from willow (17–22%) than from Pennsylvania fanpetals (12–14%). The utilisation of P from willow ash reached 10.4–13.6%, compared with 7.3–9.4% when ash from Pennsylvania fanpetals was incorporated into the soil. Willow absorbed the least magnesium added to soil with ash (3.0–5.5%) in the case of willow ash, and 0.9–2.7% when ash originated from Pennsylvania fanpetals. The absorption of nutrients from ash was generally slightly smaller than from mineral salts.

The incubation experiment included an assessment of the impact of ash produced from burning plant biomass on hydrolytic acidity and on the content of available forms of macro- and micronutrients in soil with different textural composition (Tables 7 and 8). A higher dose of ash caused a decline in the hydrolytic acidity of the analysed soils. Although the ash from burning Pennsylvania fanpetals reduced the acidity of soil slightly more than ash from willow did, the difference was not statistically

Figure 1. Use of nutrients from ashes (average from 3 years of research).
significant. According to the Polish classification [26], the content of P available forms in the soils incubated without ash was very low (11.7 mg kg\(^{-1}\) of light soil) and low in very light and medium soils (52.2 and 24.6 mg kg\(^{-1}\), respectively). The content of available K was moderate in very light and medium soils (70.8 and 137.7 mg kg\(^{-1}\), respectively) and low in light soil (65.4 mg kg\(^{-1}\)). The content of Mg was high in very light and light soil (43.6 and 58.7 mg kg\(^{-1}\), respectively), being very high in medium soil (105.1 mg kg\(^{-1}\)). The soil concentrations of available forms of P, K and Mg, irrespective of the grain-size composition of the soil, rose in parallel to the increasing doses of ash. In response to the ash being introduced to the soil, and particularly to its larger doses, the amounts of available P and K increased to the levels which justified the classification of the substrate to soils of a higher availability class. The content of available Mg, while increasing, changed to a lesser degree. Higher content of the above elements was determined in soils incubated with willow ash than with Pennsylvania fanpetals ash. Soils incubated with ash from the burning of willow contained by 58% and 47% more available forms of phosphorus and potassium, respectively, while the content of magnesium was just 9.5% higher.

Table 7. Effect of ash from plant biomass on selected properties of soil.

| Specification | Dose       | Hh    | Available Macronutrients [mg kg\(^{-1}\)] |
|---------------|------------|-------|------------------------------------------|
|               |            | [mmol(+)-kg\(^{-1}\)] | P    | K     | Mg   |
| Very light soil |            |                   |      |       |      |
| Control       | 0          | 22.5 f *         | 52.2 b | 70.8 d | 43.6 a |
| Ash from energy willow (AEW) | 0.25 Hh    | 17.2 c         | 79.4 a | 91.0 ab | 59.2 a |
|               | 0.50 Hh    | 16.5 ab        | 107.8 e | 100.0 c | 63.0 a |
|               | 1.00 Hh    | 11.2 d         | 154.6 f | 191.3 f | 66.1 a |
| Ash from Pennsylvania fanpetals (APF) | 0.25 Hh    | 19.5 e         | 62.3 c | 78.1 e | 48.8 a |
|               | 0.50 Hh    | 15.0 ab        | 77.1 a | 87.9 a | 49.0 a |
|               | 1.00 Hh    | 14.2 a         | 101.9 d | 96.3 bc | 48.4 a |
| Light soil    |            |                   |      |       |      |
| Control       | 0          | 30.7 d          | 11.7 a | 65.4 b | 58.7 c |
| Ash from energy willow (AEW) | 0.25 Hh    | 23.2 a         | 32.8 c | 91.5 b | 63.2 a |
|               | 0.50 Hh    | 24.0 a         | 51.2 e | 166.7 f | 68.9 d |
|               | 1.00 Hh    | 14.2 b         | 83.3 f | 197.4 e | 78.5 f |
| Ash from Pennsylvania fanpetals (APF) | 0.25 Hh    | 24.7 a         | 15.4 a | 72.5 c | 63.9 ab |
|               | 0.50 Hh    | 27.0 c         | 24.9 b | 82.3 d | 74.1 e |
|               | 1.00 Hh    | 15.0 b         | 41.4 d | 94.1 b | 66.3 b |
| Medium soil   |            |                   |      |       |      |
| Control       | 0          | 33.7 f          | 24.6 a | 137.7 a | 105.1 c |
| Ash from energy willow (AEW) | 0.25 Hh    | 26.2 a         | 51.9 d | 126.1 a | 111.4 a |
|               | 0.50 Hh    | 19.5 d         | 76.3 f | 206.5 b | 118.6 d |
|               | 1.00 Hh    | 12.0 b         | 130.9 h | 208.4 b | 127.6 e |
| Ash from Pennsylvania fanpetals (APF) | 0.25 Hh    | 29.2 e         | 32.5 b | 134.6 a | 114.5 b |
|               | 0.50 Hh    | 26.2 a         | 38.0 c | 133.7 a | 116.0 b |
|               | 1.00 Hh    | 15.0 c         | 64.3 e | 156.0 a | 109.5 a |
| Average for ash type | Ash from energy willow (AEW) | 20.7 A | 85.4 B | 153.2 B | 84.1 A |
|               | Ash from Pennsylvania fanpetals (APF) | 18.3 A | 50.9 A | 104.0 A | 76.7 A |

* data marked with the same letters do not differ significantly at \( p < 0.01 \).

The content of trace elements depended primarily on the agronomic category of soil (Table 8). In line with the Polish classification [27], light and medium soils incubated without ash were distinguished by a high content of Cu soluble in 1 mol HCl dm\(^{-3}\) (3.71 and 8.02 mg kg\(^{-1}\), respectively); for comparison, light soil contained an average amount of Cu (3.84 mg kg\(^{-1}\)). The content of Mn in all soils fell within a range corresponding to moderate concentrations (85.9, 61.9 and 72.8 mg kg\(^{-1}\), respectively). In turn, the content of Zn in very light soil was high (5.64 mg kg\(^{-1}\)), being average in light (5.15 mg kg\(^{-1}\)) and
medium light soils (5.53 mg kg\(^{-1}\)). Finally, the content of Fe in very light soil (557 mg kg\(^{-1}\)) and light soil was low (514 mg kg\(^{-1}\)), being average in medium light soil (1142.3 mg kg\(^{-1}\)). The applied ashes significantly, albeit to a small degree, modified the content of mobile (soluble in 1 mol HCl dm\(^{-3}\)) forms of trace elements in particular types of soil. Increasing doses of ashes had a significant effect on the concentrations of mobile forms of chromium, nickel and lead in soil, but the direction of induced changes was not unequivocal.

### Table 8. Influence of ash from plant biomass on the content of trace elements in soil.

| Specification          | Dose     | Cu mg kg\(^{-1}\) | Mn mg kg\(^{-1}\) | Zn mg kg\(^{-1}\) | Fe mg kg\(^{-1}\) | Cr mg kg\(^{-1}\) | Ni mg kg\(^{-1}\) | Pb mg kg\(^{-1}\) |
|------------------------|----------|--------------------|-------------------|-------------------|-----------------|-----------------|-----------------|-----------------|
| **Very light soil**    |          |                    |                   |                   |                 |                 |                 |                 |
| Control                | 0        | 3.71 a             | 85.9 ab           | 5.64 bc           | 557 a           | 0.33 ac         | 0.41 b          | 3.50 c          |
| Ash from energy willow (AFW) | 0.25 Hh | 3.70 a             | 82.5 a            | 5.41 a-c          | 594 bc          | 0.46 ab         | 0.32 ab         | 4.66 a          |
|                        | 0.50 Hh  | 3.70 a             | 94.9 b            | 6.13 c            | 605 c           | 0.42 a-c        | 0.19 ac         | 4.55 ab         |
|                        | 1.00 Hh  | 4.07 c             | 85.1 ab           | 6.03 c            | 579 a-c         | 0.61 b          | 0.34 ab         | 4.78 a          |
| Ash from Pennsylvania fanpetals (APF) | 0.25 Hh | 3.43 b             | 86.7 ab           | 4.32 a            | 568 ab          | 0.49 ab         | 0.34 ab         | 3.21 c          |
|                        | 0.50 Hh  | 3.69 a             | 69.5 c            | 4.78 ab           | 557 a           | 0.17 c          | 0.13 c          | 4.37 ab         |
|                        | 1.00 Hh  | 3.71 a             | 83.7 ab           | 4.71 ab           | 586 a-c         | 0.58 ab         | 0.33 ab         | 4.20 b          |
| **Light soil**         |          |                    |                   |                   |                 |                 |                 |                 |
| Control                | 0        | 3.84 a             | 61.9 b            | 5.15 b            | 514 a           | 0.16 c          | 0.16 a          | 4.17 ab         |
| Ash from energy willow (AFW) | 0.25 Hh | 3.94 a             | 76.2 ac           | 4.08 a            | 548 ab          | 0.31 b          | 0.19 a          | 4.22 a          |
|                        | 0.50 Hh  | 4.18 b             | 66.3 ab           | 4.33 a            | 517 a           | 0.33 b          | 0.39 b          | 4.25 a          |
|                        | 1.00 Hh  | 4.68 c             | 77.8 a            | 5.10 b            | 600 b           | 0.30 b          | 0.28 ab         | 4.55 a          |
| Ash from Pennsylvania fanpetals (APF) | 0.25 Hh | 3.88 a             | 60.8 b            | 3.75 a            | 506 a           | 0.19 ac         | 0.26 ab         | 4.46 b          |
|                        | 0.50 Hh  | 3.94 a             | 77.5 a            | 3.82 a            | 564 ab          | 0.24 a          | 0.20 a          | 3.73 a          |
|                        | 1.00 Hh  | 4.13 b             | 82.1 a            | 3.96 a            | 583.8 b         | 0.24 a          | 0.21 a          | 4.22 a          |
| **Medium soil**        |          |                    |                   |                   |                 |                 |                 |                 |
| Control                | 0        | 8.02 a             | 72.8 a-c          | 5.53 ab           | 1142 b          | 0.71 b          | 1.09 a          | 5.57 a          |
| Ash from energy willow (AFW) | 0.25 Hh | 7.62 b             | 63.2 c            | 4.95 acd          | 998 c           | 0.51 a          | 1.04 a          | 4.92 ab         |
|                        | 0.50 Hh  | 7.87 ab            | 75.1 ab           | 5.34 abd          | 1059 a-c        | 0.54 a          | 1.02 a          | 4.95 ab         |
|                        | 1.00 Hh  | 8.10 a             | 80.0 a            | 5.93 b            | 1066 a-c        | 0.51 a          | 0.70 b          | 4.87 ab         |
| Ash from Pennsylvania fanpetals (APF) | 0.25 Hh | 8.07 c             | 67.8 bc           | 5.54 ab           | 1031 ac         | 0.80 b          | 0.90 ab         | 5.39 a          |
|                        | 0.50 Hh  | 8.11 a             | 82.4 a            | 4.71 cd           | 1108 b          | 0.79 b          | 0.97 a          | 4.08 b          |
|                        | 1.00 Hh  | 7.99 a             | 74.1 ab           | 4.63 c            | 1111 b          | 0.46 a          | 1.09 a          | 5.17 a          |
| Average for ash type   |          |                    |                   |                   |                 |                 |                 |                 |
| Ash from energy willow (AFW) |        | 5.32 a             | 77.9 a            | 5.26 b            | 735 a           | 0.44 a          | 0.50 a          | 4.64 b          |
| Ash from Pennsylvania fanpetals (APF) | 5.31 a | 76.1 a             | 4.47 a            | 729 a             | 0.44 a          | 0.49 a          | 4.31 a          |

* data marked with the same letters do not differ significantly at p < 0.01.

When comparing the effects of both types of ash, it could be noticed that soils incubated with willow ash contained more Zn and Pb (by 17.7% and 7.7%, respectively) than soils incubated with ash from Pennsylvania fanpetals.

A properly selected dose of biomass ash can improve the chemical properties of soil, including its pH, increase the content of available forms of macroelements and microelements for plants, and reduce the concentration of mobile forms of heavy metals, such as Pb and Cd [28]. Decacidification of soil caused by ash is a consequence of the content of potassium, calcium and magnesium oxides in this substance [29,30]. According to Cruz-Paredes et al. [31], using biomass ash in agriculture could be an example of a sustainable strategy of maintaining the phytoavailable P resources in soils. In incubation experiments conducted by Quirantes et al. [32], it was demonstrated that biomass ash was able to raise considerably the soil’s pH, electrical conductivity, and activity of dehydrogenase. Ash from the residue left from olive oil production was more effective in the improvement of soil with regard to its content of available (AB-DTPA extractable) forms of P, K and Cu. In turn, ash from wood caused the greatest increase in the content of soil-extractable Zn. Schiemenz and Eichler-Löbermann [33] as well as Schiemenz et al. [5] maintain that the water solubility of P found in biomass ash was low; however, approximately 80% of P was extractable in citric acid. In general, the fertilising effect of P from the
ashes was comparable with the impact of readily soluble phosphorus fertilisers. The application of ash caused an increase in the uptake of P by crops and a higher content of P in soil (P-total, water soluble P, lactate soluble P, P soluble in oxalates). Exact effects produced by the application of ash to soil also depended on crops grown in that soil. Piekarczyk [34] demonstrated that as doses of ash from winter wheat straw were increased (from 0 to 1.0 t ha\(^{-1}\)), a tendency appeared towards a higher soil pH and richness in available forms of macro- and micronutrients. This researcher claims that winter wheat straw ash can be considered as a good and inexpensive potassium fertiliser with alkaline reaction. Karps et al. [35] report that biomass ash is suitable for use as fertiliser supplied to soils poor in phosphorus and potassium but rich in nitrogen. In turn, when ash is granulated with slurry, it becomes a fertiliser that supplies plants with essential nitrogen, in addition to which the granulated form prevents the problem of dust emission during transport and application. The content of P, K, Mg, S and Zn in soil increased significantly after the application of wood ash [12].

In a previous study, Wierzbowska et al. [25] found that ash generated from the incineration of sewage sludge and used as a substitute of phosphorus fertilisers did not have any significant effect on the soil content of mobile forms of Cd, Cu, Pb and Cr, whereas higher doses of this waste resulted in a considerable increase in the soil concentrations of Zn, Ni and Mn. In the second season following the application of ash, Cruz-Paredes et al. [31] did not observe any undesirable side effects regarding yields of grown crops, nutrition, accumulation of Cd in plants or the mycorrhizal status. After an application of ashes, the soil content of available P forms was similar to the one achieved by using popular phosphorus fertilisers. Ashes from the biomass did not have any adverse effect on the colonisation or activity of mycorrhizal fungi. The enrichment of soil with wood ash resulted in higher concentrations of nutrients in both the soil and plants, while the increased soil pH inhibited the mobility of potentially toxic elements and limited their uptake by plants [36]. Łapiński et al. [37] showed that while heavy metals in digestate occurred mainly in mobile fractions, in ashes, owing to thermal treatment, they were predominantly fixed in non-mobile forms.

4. Conclusion

The results of the experiments presented in this paper justify the claim that ash generated from burning willow or Pennsylvania fanpetals can be applied instead of phosphorus, potassium and magnesium fertilisers in the cultivation of energy willow. The effect of these two types of ash on willow yield and the yield content of essential nutrients was similar to that achieved when soil had been fertilised with equivalent amounts of the same elements in the form of mineral salts. The plant uptake of P, K and Mg from ashes also did not diverge from their absorption by plants when supplied in mineral salts. It is therefore our opinion that the tested ashes could be successfully used in cultivation of the other energy crops. One should also appreciate the strong deacidifying properties of the tested ashes, and their beneficial effect on the soil content of phytoavailable forms of phosphorus, potassium and, to a slightly smaller extent, of magnesium. Moreover, ash from the incineration of willow or Pennsylvania fanpetals can also improve the availability of micronutrients in the soil (Cu and Fe), although attention should be paid to the minimally higher content of Pb under the influence of ash from the burning of willow.

Author Contributions: Conceptualization, S.S. and J.W., Methodology, S.S. and J.W., Data curation, J.W., Formal analysis, P.Z. and S.K.; Project administration, S.S.; Supervision, J.W.; Writing—original draft, J.W.; Writing—review and editing, S.S. and J.W. All authors have read and agreed to the published version of the manuscript.

Funding: The project was financially supported by the Minister of Science and Higher Education in the range of the program entitled “Regional Initiative of Excellence” for the years 2019–2022, Project No. 010/RID/2018/19, amount of funding 12.000.000 PLN. This work was also supported by the Innovative Economy Operational Program EU [Key Project No. POIG.01.01.02-00-016/08].

Conflicts of Interest: The authors declare no conflict of interest.
References

1. GUS. Energy from Renewable Resources in 2017; Polish Main Statistical Office (GUS) Report of 2018; GUS: Warsaw, Poland, 2018. Available online: https://stat.gov.pl/obszary-tematyczne/srodowisko-energia/energia-ze-zrodzel-odnawialnych-w-2017-roku,10,1.html# (accessed on 10 November 2019).

2. Baum, R.K.; Pepliński, B.; Wawrzyńcowicz, J. Potential for Agricultural Biomass Production for Energy Purposes in Poland: A Review. Contemp. Econ. 2013, 7, 63–74. [CrossRef]

3. Stolarski, M.J.; Niksa, D.; Krzyżaniak, M.; Tworkowski, J.; Szczykowski, S. Willow productivity from small- and large-scale experimental plantations in Poland from 2000 to 2017. Renew. Sustain. Energy Rev. 2019, 101, 461–475. [CrossRef]

4. Rajamma, R.; Ball, R.; Tarelho, L.; Allen, G.; Labrincha, J.; Ferreira, V. Characterisation and use of biomass fly ash in cement-based materials. J. Hazard. Mater. 2009, 172, 1049–1060. [CrossRef] [PubMed]

5. Schiemenz, K.; Kern, J.; Paulsen, H.-M.; Bachmann, S.; Eichler-Löbermann, B. Phosphorus fertilizing effects of biomass ashes. In Recycling of Biomass Ashes; Insam, H., Knapp, B.A., Eds.; Springer: Berlin, Germany, 2011; pp. 17–31.

6. 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]

7. Pesonen, J.; Kuokkanen, T.; Rautio, P.; Lassi, U. Bioavailability of nutrients and harmful elements in ash fertilizers: Effect of granulation. Biomass Bioenergy 2017, 100, 92–97. [CrossRef]

8. Pitman, R.M. Wood ash use in forestry–a review of the environmental impacts. Forests 2016, 50, 139–144. (In Polish) [CrossRef]

9. Saletnik, B.; Zaguła, G.; Bajcar, M.; Czernicka, M.; Puchalski, C. Biochar and Biomass Ash as a Soil Ameliorant: Their Agricultural Use. Przemysł Chemiczny 2017, 96, 2501–2504. (In Polish) [CrossRef]

10. Sumara, A.; Stankowski, S.; Gołąbowski, W.; Szczepanik, M. Chemical Characteristics of Biomass Ashes. Energies 2018, 11, 2885. [CrossRef]

11. Zając, G.; Szyszak-Bargłowicz, J.; Gołąbowski, W.; Szczepanik, M. Chemical Characteristics of Biomass Ashes. Energies 2018, 11, 2885. [CrossRef]

12. Szafran, E.; Pepliński, B.; Hrubiaj, P. Introduction of Fertilizers on the Commercial Market. Available online: http://www.iung.pulawy.pl/index.php?option=com_content&view=article&id=99&Itemid=61 (accessed on 10 November 2019). (In Polish).

13. Polskie Towarzystwo Gleboznawcze. Particle size distribution and textural classes of soils and mineral materials-classification of Polish Society of Soil Science 2008. Roczn. Glebozn. 2009, 60, 5–16. Available online: http://ssa.ptg.sggw.pl/files/artykuly/2009_60/2009_tom_60_2/tom_60_2_005-016.pdf (accessed on 10 November 2019). (In Polish).
22. Ostrowska, A.; Gawliński, S.; Szczubiałka, Z. Methods of Analysis and Assessment of Soil and Plant Properties; Institute of Environmental Protection: Warsaw, Poland, 1991; 334p. (In Polish)

23. Lindvall, E.; Gustavsson, A.-M.; Samuelsson, R.; Magnusson, T.; Palmberg, C. Ash as a phosphorus fertilizer to reed canary grass: Effects of nutrient and heavy metal composition on plant and soil. *Glob. Chang. Biol. Bioenergy* 2015, 7, 553–564. [CrossRef]

24. Li, X.; Rubæk, G.H.; Sørensen, P. High plant availability of phosphorus and low availability of cadmium in four biomass combustion ashes. *Sci. Total Environ.* 2016, 557–558, 851–860. [CrossRef]

25. Wierzbowska, J.; Sienkiewicz, S.; Sternik, P.; Busse, M.K. Using Ash from Incineration of Municipal Sewage Sludge to Fertilize Virginia Fanpetals. *Ecol. Chem. Eng. A* 2015, 22, 497–507. [CrossRef]

26. Saletnik, B.; Bajcar, M.; Zagula, G.; Czernicka, M.; Puchalski, C. Influence of biochar and biomass ash applied as soil amendment on germination rate of Virginia mallow seeds (*Sida hermaphrodita* R.). *Econtechmod Int. Q. J.* 2016, 5, 71–76.

27. Fertilisation Recommendations. *Threshold Amounts for Assessment of Soil Content of Macro- and Micronutrients*; Series P44; Publishing House IUNG: Pulawy, Poland, 1990; 26p. (In Polish)

28. Saletnik, B.; Puchalsk, C. Suitability of Biochar and Biomass Ash in Basket Willow (*Salix Viminalis* L.) Cultivation. *Agronomy* 2019, 9, 577. [CrossRef]

29. Piekarczyk, M.; Kotwica, K.; Jaskulski, D. The elemental composition of ash from straw and hay in the context of their agricultural utilization. *Acta Sci. Pol. Agric.* 2011, 10, 97–104.

30. Wacławowicz, R. The effect of ashes from biomass combustion on infection of spring wheat by *Gaeumannomyces graminis*. *Prog. Plant Prot.* 2012, 52, 397–400.

31. Cruz-Paredes, C.; López-García, Á.; Rubæk, G.H.; Hovmand, M.F.; Sørensen, P.; Kjøller, R. Risk assessment of replacing conventional P fertilizers with biomass ash: Residual effects on plant yield, nutrition, cadmium accumulation and mycorrhizal status. *Sci. Total Environ.* 2017, 575, 1168–1176. [CrossRef]

32. Quirantes, M.; Calvo, F.; Romero, E.; Nogales, R. Soil-nutrient availability affected by different biomass-ash applications. *J. Soil Sci. Plant Nutr.* 2016, 16, 159–163. [CrossRef]

33. Schiemenz, K.; Eichler-Löbermann, B. Biomass ashes and their phosphorus fertilizing effect on different crops. *Nutr. Cycl. Agroecosyst.* 2010, 87, 471–482. [CrossRef]

34. Piekarczyk, M. Effect of winter wheat straw ash on the some macro- and microelements available forms content in light soil. *Fragm. Agron.* 2013, 30, 92–98. (In Polish)

35. Karps, O.; Aboltins, A.; Palabinskis, J. Biomass ash utilization opportunities in agriculture. In Proceedings of the 8th International Scientific Conference Rural Development, Kaunas, Lithuania, 23–25 November 2017; Raupeliėnė, A., Ed.; Aleksandras Stulginskis University: Kaunas, Lithuania, 2017; pp. 193–198. [CrossRef]

36. Ochecova, P.; Tlustos, P.; Szakova, J. Wheat and Soil Response to Wood Fly Ash Application in Contaminated Soils. *Agron. J.* 2014, 106, 995–1002. [CrossRef]

37. Łapiński, D.; Water, J.; Szatyłowicz, E. The Content of Heavy Metals in Waste as an Indicator Determining the Possibilities of Their Agricultural Use. *J. Ecol. Eng.* 2019, 20, 225–230. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).