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Suitability of Biochar and Biomass Ash in Basket Willow (*Salix Viminalis* L.) Cultivation

Bogdan Saletnik * and Czesław Puchalski

Department of Bioenergy Technology, Faculty of Biology and Agriculture, Rzeszow University, Ćwiklińskiej 2D, 35-601 Rzeszow, Poland; cpuchal@ur.edu.pl

* Correspondence: bogdan.saletnik@urz.pl; Tel.: +48-17-785-49-65

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Abstract: The article presents the findings of a field experiment investigating the effectiveness of biochar and plant biomass ash when used as a soil fertiliser in the cultivation of basket willow (*Salix viminalis* L.). The purpose of the study was to determine the optimal dose of fertiliser to enable a maximum increase in the crop yield and enhancement of the chemical properties of the soil. In the course of the two-year experiment, the increase in basket willow yield was in the range of 6%–49%. The highest dry matter yield from the plants, at the end of both the first and the second year of the experiment, was obtained in the plots where the soil was amended with biochar alone (11.5 t ha^{-1}), a combination of biochar and ash (respectively 11.5 and 1.5 t ha^{-1}) and ash added at the rate of 1.5 t ha^{-1}. The yield was reduced when the soil was amended with ash added at the rates of 3.0 t ha^{-1} and 4.5 t ha^{-1} or with the latter doses of ash combined with biochar. The results indicated that too high a concentration of ash (rate of 3.0 t ha^{-1} or higher for basket willow) have negative effects on plant growth and may represent a limiting factor. The study suggests that biochar is a better soil amendment than ash, because biochar application gave the highest improvement in the soil properties and plant growth. It was found that the addition of biochar, biomass ash or combinations of the two materials applied in suitable doses may be a good soil amendment.. In particular in soils which are severely damaged and require restoration, this fertilization may have a noticeable effect on soil properties and plant growth.

Keywords: biochar; biomass ash; soil amendment; basket willow

1. Introduction

Biochar, or more precisely, its broad applicability, may constitute a solution to increasing environmental problems, such as severe climate change and soil degradation, decreasing non-renewable energy resources, and the requirements for sustainable waste management [1]. In recent years numerous publications have reported a positive impact of biochar on soil fertility. Biochar is carbonised organic matter of plant or animal origin which is incorporated into soils in order to improve their characteristics [2]. Properties of biochars depend on the input biomass and the pyrolysis parameters applied in the production process. Biochars are resistant to degradation and biological decomposition, and when added to soils they are highly stable in terms of their chemical composition; and because of this they are thought to be a highly effective vehicle for carbon dioxide sequestration in the soil [3]. The stability of biochar in soil depends on the type of substrate used in its production, the parameters of the pyrolysis process as well as the soil characteristics and climate conditions [1,4]. Carbon stored in soil amended with biochar may remain there for hundreds or even thousands of years [5–7]. Greenwaste biochars comprise macro- and micro-elements which are a valuable source of minerals (e.g., calcium, magnesium, phosphorus, potassium, and carbonates) for plants and soil microorganisms [8]. Owing to their large ion-exchange capacity and specific surface, biochars reduce the loss of biogenic elements in the soil and contribute to decreased emissions of N_2O and CH_4 from soil [1,9]. Biochars are characterised by a highly porous internal structure which affects water absorbability, sorption capacities, as well as the retention and exchange of nutrients in the soil [10,11]. They also affect the physical properties of soil, promoting the formation of soil aggregates, increasing the resistance of soil to erosion, improving its water-holding capacity, and increasing soil pH [12,13].

Natural fertilisers used by humans, even in prehistoric times, have included ashes [14,15]. The ash produced in the process of plant biomass combustion contains macro- and micro-elements necessary for plant growth and when used as a soil amendment it may enhance the physicochemical characteristics of soil and improve crop yield. Biomass ash is characterised by alkalinity and varied contents of elements [16–20], however, it is important to note that it may also contain elevated levels of heavy metals [21,22]. Owing to its high pH and the low cost of acquiring such material, biomass ash may be an alternative to traditional deacidification agents.

Basket willow (*Salix viminalis* L.) also known as common osier, or simply osier, is a perennial plant, one of those most commonly used for energy-related purposes. It grows in Europe, Asia and North America. Basket willow is a fast-growing species and is highly resistant to pests and diseases [23,24]. As an energy crop, it is harvested in one-, two- or three-year cycles [25]. During the first year of growth biomass productivity is very low, due to the fact that the plant is rapidly developing its root system, at the expense of the aboveground part. Willow shoots may effectively be harvested at the end of the second year of its growth. In field cultivation, vegetative reproduction is used [26–28]. Areas with class III, IV and V soils with sufficient moisture levels can be readily used for willow cultivation [29]. Insufficient water levels during growth adversely affect the development of root systems [30]. Out of the numerous willow species, the most effective energy crops include basket willow *Salix viminalis* L., and its hybrid cultivars [31]. Analyses focusing on willow productivity should take into account the fact that the yield depends on a number of factors, such as the willow cultivar and clone selected, crop density, agricultural treatments applied, harvesting frequency as well as soil and weather conditions.

The study was designed to assess the effectiveness of soil amendment based on biochar and ash from plant biomass combustion, and applied in the cultivation of basket willow (*Salix viminalis* L.). Additionally, an attempt was made to determine the optimal dose of various combinations of the fertilisers.

2. Materials and Methods

2.1. Site Description

Two-year field trials were conducted in Krasne (Subcarpathian Voivodship, Poland, 50°04′16.1′′ N, 22°04′37.6′′ E) over the period 2015–2017. They were located on arable land of the IVb land quality class (soil by a limited selection of arable crops, too dry or too moist, exposed to water erosion, gives average yields despite the use of good agricultural technology, yields vary widely and are very dependent on weather conditions [32]) in a split-block system in four repetitions. The total number of plots in the field experiment was 32; the area of each was 35 m^2 (7 m length, 5 m width) and for the harvest 24 m^2 (6 m length, 4 m width). According to agricultural suitability, soil corresponded to the defective wheat complex. According to agricultural usefulness, soil is classified as defective wheat complex. These are soils with a concise granulometric composition, incapable of storing more water, periodically too dry, despite the worse water conditions and smaller humus level, they keep good physical properties [33]. Meteorological conditions were determined based on data from a meteorological station located in Rzeszow city. Large disproportions between the annual rainfall for the year 2015 and 2016 were found, which were at 471 and 721 mm respectively. The average annual air temperature measured at the meteorological station was 10.2 °C in 2015 and 9.4 °C in 2016.

2.2. Experimental Design

The area covered by the research was agricultural fallow left without any intervention for more than 10 years. In order to prepare the soil for cultivation (autumn 2013), mulching was performed with a brush cutter, followed by weeding in the form of a Roundup 360 SL spray (dose: 6 L ha^{-1}); after two weeks, disc ploughs and deep ploughing were performed using a mouldboard plough. In the spring of 2015, treatments for improving the soil (levelling the land surface, breaking up the soil lumps and destroying emerging weeds) were performed in the form of harrowing and the use of a passive tillage aggregate. Based on the results of analyses performed before the experiment and the nutritional needs of plants, recommendations for fertiliser application were developed. Fertiliser treatments with biochar at a dose of 11.5 t ha^{-1}, ash from biomass at doses of 1.5, 3.0, 4.5 t ha^{-1} and a combination of these were used. In April 2015, fertilisers were sown manually, and then mixed with the soil to a depth of approximately 20 cm by means of a rototiller. Seedlings of basket willow were obtained from a private supplier (Podkarpackie Voivodship, Poland). On 16 April 2015, seedlings were manually planted on the experimental plots: planting depth: 18 cm (cuttings 20 cm in length); spacing of seedlings: 0.33 m; spacing of rows: 0.7 m; density: 40,000 plants ha^{-1}. The biomass harvest from the plots was performed in February 2016 and 2017 using a brush cutter with a cutting disc, rejecting extreme rows (height of the cut above the soil surface—10 cm). In the second year of the experiment, no re-application of fertiliser in the form of biochar and ash from biomass was carried out.

2.3. Fertiliser Material

The biochar, in the form of coal scales, originated from the processing of biomass from energy crops (commercially available, Poland). The biochar used in the study was characterised by a pH value of 6.59 with total contents of carbon and nitrogen amounting to 74.35% and 0.93%, respectively. The tests also showed the water and ash content of the biochar being at a level of 9.11% and 11.57%, respectively. The biochar was characterised by a high content of volatile substances, i.e., 66.42%. The fertiliser material in the form of ash from the combustion of a mixture of biomass from energy crops and plant biomass of agricultural origin was obtained from the Tauron power station (Stalowa Wola, Poland). Biochar was subjected to a grinding process with the use of the Laarmann CM-1000 high-speed cutting mill (Laarmann Group B.V., Roermond, Netherlands). The grinding process was performed using a sieve with a mesh size of 10 mm. Ash generated from the combustion of plant biomass did not require additional treatment before its application.

2.4. Biomass Production

The yield of plants was assessed at the end of each growing season. The plant material collected was dried at 70 °C, weighed and the biomass yield of dry matter in t ha^{-1} was calculated.

2.5. Examination of Samples

Samples of soil, biochar, ash from biomass and the aboveground parts of giant basket willow plants were subjected to laboratory analyses using current analytical standards (Table 1).

The determination of the pH of the study materials was performed by measuring the concentration of hydrogen ions, i.e., the activity of hydrogen ions (H^+) with the use of the potentiometric method. The analysis was performed in KCl solution with a concentration of 1 mol dm^{-3}, assuming a mass ratio of the study sample to solution volume of 1:2.5. Measurements were performed using the Nahita pH meter, model 907 (AUXILAB, Beriáin, Spain).

Analyses of the contents of ash and volatile substances in the study materials using thermogravimetric methods were performed using the TGA 701 apparatus by LECO (LECO Corporation, Saint Joseph, MI, USA). The content of total carbon and nitrogen was tested using the TrueSpec CHN analyser by LECO (LECO Corporation, Saint Joseph, MI, USA). The AC500 calorimeter by LECO (LECO Corporation, Saint Joseph, MI, USA) was used to determine the calorific value of the materials analysed.

Table 1. Parameters analysed with research methods.

Item	Parameter	Research Method
1.	pH in KCl	PN-ISO 10390:1997 [34]
2.	Content of absorbable forms of phosphorus (P_2O_5)	PN-R-04023:1996 [35]
3.	Content of absorbable forms of potassium (K_2O)	PN-R-04022:1996/Az1:2002 [36]
4.	Content of absorbable form of magnesium (Mg)	PN-R-04020:1996/Az1:2004 [37]
5.	Content of carbon, nitrogen and hydrogen	PN-EN 15104:2011 [38]
6.	Ash content	PN-EN 14775:2010 [39]
7.	Content of volatile substances	PN-EN 15148:2011 [40]
8.	Calorific value	PN-EN 14918:2010 [41]
9.	Total content of selected macro and microelements	Method using atomic emission spectrometry with excitation in argon plasma (inductively coupled plasma atomic emission spectroscopy ICP—OES)

The mineralisation of the study material was performed in three repetitions. The contents of the elements in the samples were determined using a method based on inductively coupled plasma atomic emission spectroscopy (ICP-OES), with the use of the iCAP Dual 6500 analyser (Thermo Fisher Scientific, Schaumburg, IL, USA). The mineralisation of the study samples was performed in Teflon containers using a mixture of acids under specific conditions (Table 2). In each case, a 0.2 g sample was mineralised. The sample obtained in this way was supplemented with mineralised water to make a volume of 50 mL. In the calibration step, standard solutions for all elements were prepared from the spectroscopic grade reagent (Thermo Fisher Scientific, Cambridge, UK) with a three-step curve. The curve fit factor for all elements was over 0.99. Selection of a measuring line of appropriate length was validated by the method of standard additions. The recovery on selected lines was above 98.5% for each of the elements. Each time, the CRM 1515 (Certified Reference Material, Thermo Fisher Scientific, Cambridge, UK) was used and the selection of appropriate lines was implemented using the standard addition method. Each time we also used internal standards for matrix curve correction; these were yttrium (Y) and ytterbium (Yb), two elements not detected in the samples. The detection limit of the analytical method used for the elements studied was no worse than 0.01 mg kg^{-1} [42].

Table 2. Parameters of the mineralisation process.

Material	Acid	Temperature and Time	Power	Application Note
Soil	8 mL HNO_3 65% 5 mL HCl 37% 1 mL HF 40% 5 mL H_3BO_3 5%	temperature increase to 200 °C, time: 15 min; maintaining at temperature of 200 °C, time: 15 min	1500 W	HPR-EN-13 [43]
Biochar	7 mL HNO_3 65% 1 mL H_2O_2 30%			HPR-PE-19 [44]
Plant Biomass	6 mL HNO_3 65% 2 mL H_2O_2 30%			HPR-AG-02 [45]
Ash from biomass	7 mL HNO_3 65% HCl 37% 1.5 HF 40%	temperature increase to 220 °C, time: 20 min; maintaining at temperature of 220 °C, time: 15 min		HPR-EN-04 [46]

2.6. Names of Tests

The tests used for further identification are described by symbols, due to the type and application rate of the fertiliser used:

- B1/P1 (control test—no fertiliser);
- P2 (fertilised with ash at a dose of 1.5 t ha^{-1});
- P3 (fertilised with ash at a dose of 3.0 t ha^{-1});
- P4 (fertilised with ash at a dose of 4.5 t ha^{-1});
- B2/P1 (fertilised with biochar at a dose of 11.5 t ha^{-1});
- B2/P2 (fertilised with biochar and ash at doses of 11.5 and 1.5 t ha^{-1}, respectively);
- B2/P3 (fertilised with biochar and ash at doses of 11.5 and 3.0 t ha^{-1}, respectively);
- B2/P4 (fertilised with biochar and ash at doses of 11.5 and 4.5 t ha^{-1}, respectively).

2.7. Statistical Analyses

The verification of the influence of the experimental factors used on the parameters analysed and existing dependencies was performed using analysis of variance (ANOVA) by means of the Bonferroni post hoc test. A materiality level of ≤0.05 was applied. Analyzes were performed using a linear model. The applicable assumptions for ANOVA analyses has been tested, the groups of samples meet the normal distribution assumptions. Principal component analysis (PCA) was also applied. The primary variables used in the PCA analysis was the total content of macro- and micro-elements in soil and plants biomass. This indirect ordination technique allows one to analyse a large number of variables to detect structure and regularity in relationships between them. The scree plot and the Kaiser criterion were applied to select the number of principal components. Statistical analyses were performed using Statistica 12 software (StatSoft Polska, Krakow, Poland).

3. Results

3.1. Biochar and Biomass Ash

As a result of the tests conducted it was possible to determine the basic parameters for the natural fertilisers used in the experiment. The biochar applied in the experiment was characterised by a pH of 6.59, while the pH of the ash was 12.89. The ash from the biomass was found with contents of total carbon and total nitrogen amounting to 1.22% and 0.17%, respectively. The total contents of carbon and nitrogen in the biochar were significantly higher, amounting to 74.35% and 1%, respectively. The ash was found to be rich in absorbable forms of phosphorus, potassium and magnesium, the contents of these elements being, respectively, 4.6, 15.8 and 48.7 times higher than observed in the biochar (Table 3). Water and ash contents in the biochar totalled at 9.11% and 11.57%, respectively. High contents of volatile substances were identified in both biochar (66.42%) and biomass ash (94.42%) (Table 4).

Table 3. Value of pH, contents of absorbable forms of macro-elements, as well as percent contents of carbon and nitrogen in the biochar and biomass ash.

	pH (KCl)	**Carbon**	**Nitrogen**	**P_2O_5**	**K_2O**	**Mg**
		%		**mg kg^{-1}**		
				x ± SD		
Biochar	6.59 ± 0.21	74.35 ± 0.24	0.93 ± 0.07	1382 ± 41	5752 ± 63	645 ± 22
Ash	12.89 ± 0.32	1.22 ± 0.22	0.17 ± 0.01	6394 ± 52	91143 ± 94	31406 ± 74

x means mean, SD means standard deviation.

Table 4. Contents of water, ash and volatile substances in the biochar and biomass ash.

	Water	Ash	Volatile Substances
	%		
	x ± SD		
Biochar	9.11 ± 0.03	11.57 ± 0.21	66.42 ± 0.18
Ash	-	-	94.42 ± 0.27

x means mean, SD means standard deviation.

Table 5 shows the contents of the elements assayed in the fertilisers. Ash from the biomass obtained from the energy crop had higher contents of all the elements. Given the fact that soil amendments may contain toxic metals, the fertilising materials were examined for their heavy metal contents. The findings show that the biochar and the biomass ash contained no aluminium, arsenic, cadmium or lead.

Table 5. Contents of selected macro- and micro-elements in the biochar and biomass ash.

	Al	As	Ca	Cd	Cr	Cu	Mn
	mg kg^{-1}						
	x ± SD						
Biochar	< 0.01	< 0.01	18520 ± 21	< 0.01	< 0.01	10 ± 0.8	240 ± 2.5
Ash	< 0.01	< 0.01	131220 ± 35	< 0.01	50 ± 0.9	110 ± 0.7	1930 ± 9.5
	Mo	**Na**	**Ni**	**Pb**	**S**	**Sr**	**Zn**
	mg kg^{-1}						
	x ± SD						
Biochar	< 0.01	< 0.01	< 0.01	< 0.01	880 ± 12	< 0.01	130 ± 11.5
Ash	< 0.01	< 0.01	40 ± 2.5	< 0.01	19710 ± 23	< 0.01	710 ± 8.2

x means mean, SD means standard deviation.

3.2. Soil

Figure 1 presents soil pH in 2015, before the basket willow cultivation was started, and in 2016 as well as 2017, in relation to the type of fertiliser applied. The samples of soil in the field at the start of the experiment were found to have a pH of 4.98. The pH value in the control samples at the end of the first year of the experiment was 5.19, and after the second year decreased to 5.10. These findings show there were no statistically significant differences in this parameter between the control group and the result identified prior to the experiment. Introduction of the fertilising agents, i.e., biochar, ash and their combinations, led to a significant increase in soil pH, compared to the pH value identified before the experiment (13 out of the 16 cases investigated). The increase in pH was related to the fertiliser applied and its dose. The findings show an increase in soil pH in the range of 0.46–1.05 following the first year, and 0.04–1.05 following the second year of basket willow cultivation, compared to the control group. The most visible effects related to the alkalinisation of soils following the first and the second year of basket willow cultivation were identified in the case of fertilisation with a combination of biochar and ash at a rate of 3.0 t ha^{-1} (pH 6.1 and 6.24) as well as biochar and ash at a rate of 4.5 t ha^{-1} (pH 6.07 and 6.1)

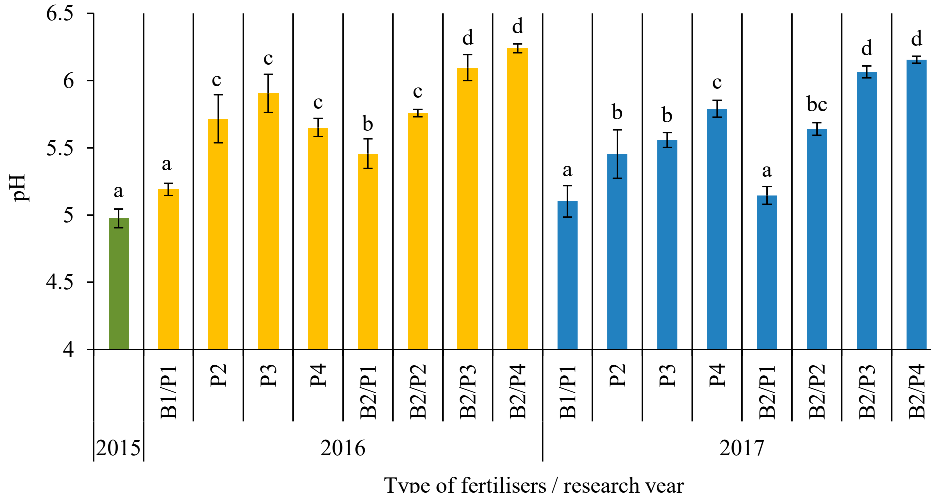


Figure 1. Values of soil pH prior to the experiment (2015) as well as following the first and the second year of cultivation in relation to the fertiliser applied. The mean values marked with the same letter do not differ significantly at a level of $\alpha \leq 0.05$ based on the results of the Bonferroni test.

Figure 2 presents the contents of absorbable forms of phosphorus, potassium and magnesium in the soil before the experiment was started, and during the two consecutive years of basket willow cultivation, depending on the type of fertiliser applied. Before the field experiment was established, the following contents of absorbable forms of the elements were identified in the soil samples: phosphorus 48 mg kg^{-1}, potassium 90 mg kg^{-1}, magnesium 95 mg kg^{-1}. At the end of the first year of cultivation, soil samples from the control plots were found to contain the following concentrations of the absorbable forms of the elements: P_2O_5 66.26 mg kg^{-1}; K_2O 97 mg kg^{-1}; and Mg 87.5 mg kg^{-1}. In most cases the doses of fertiliser applied produced statistically significant effects in the contents of the relevant elements in the soils compared to the control sample; these assumed values in the following ranges: P_2O_5 85.75–175.58 mg kg^{-1}; K_2O 138.75–342.50 mg kg^{-1}; Mg 89.25–147.25 mg kg^{-1}. The largest increase in the contents of the elements was identified in plots fertilised with a combination of biochar and ash applied at a rate of 4.5 t ha^{-1}. Compared to the control sample, the concentrations increased by 165% (phosphorus), 253% (potassium), 68% (magnesium). During the subsequent year of basket willow growth, the contents of P_2O_5, K_2O, and Mg in the soil samples from the control plots amounted to 58.75; 99.25 and 91 mg kg^{-1}, respectively. There was a decrease in the contents of absorbable phosphorus, and a small increase in the levels of potassium and magnesium, compared to year 2016. Fertilisers of various types influenced concentrations of the relevant elements producing effects in the following ranges: P_2O_5 68.00–131.25 mg kg^{-1}; K_2O 171.50–330.00 mg kg^{-1}; and Mg 111.00–158.00 mg kg^{-1}. As in the first year of the experiment, the greatest increase in the concentration of the absorbable forms of the elements resulted from the addition of the highest dose of biochar combined with ash. Compared to the control sample, the increase in the contents of the elements was as follows: phosphorus 123%, potassium 232%, and magnesium 74%.

Figure 3 presents percentage contents of total carbon, hydrogen and total nitrogen in the soil, before the experiment and at the end of each subsequent year of cultivation in relation to the type of fertiliser applied. Before the field experiment, the soil samples contained 0.64% of carbon. In 2016, at the end of the first year of basket willow growth, the contents of carbon in the soil from the control plots increased to 3.76%. After the subsequent year of the experiment the contents of carbon decreased to 3.45%. The introduction of ash as a fertiliser did not produce a significant effect in the concentration of carbon in the soil when compared to the control sample at the end of the first and second years of the experimental cultivation. Conversely, the addition of biochar or a combination of biochar and ash resulted in an increased level of total carbon in the soil. The findings showed the highest concentrations of 4.5% after the first, and 3.88% after the second year of basket willow growth.

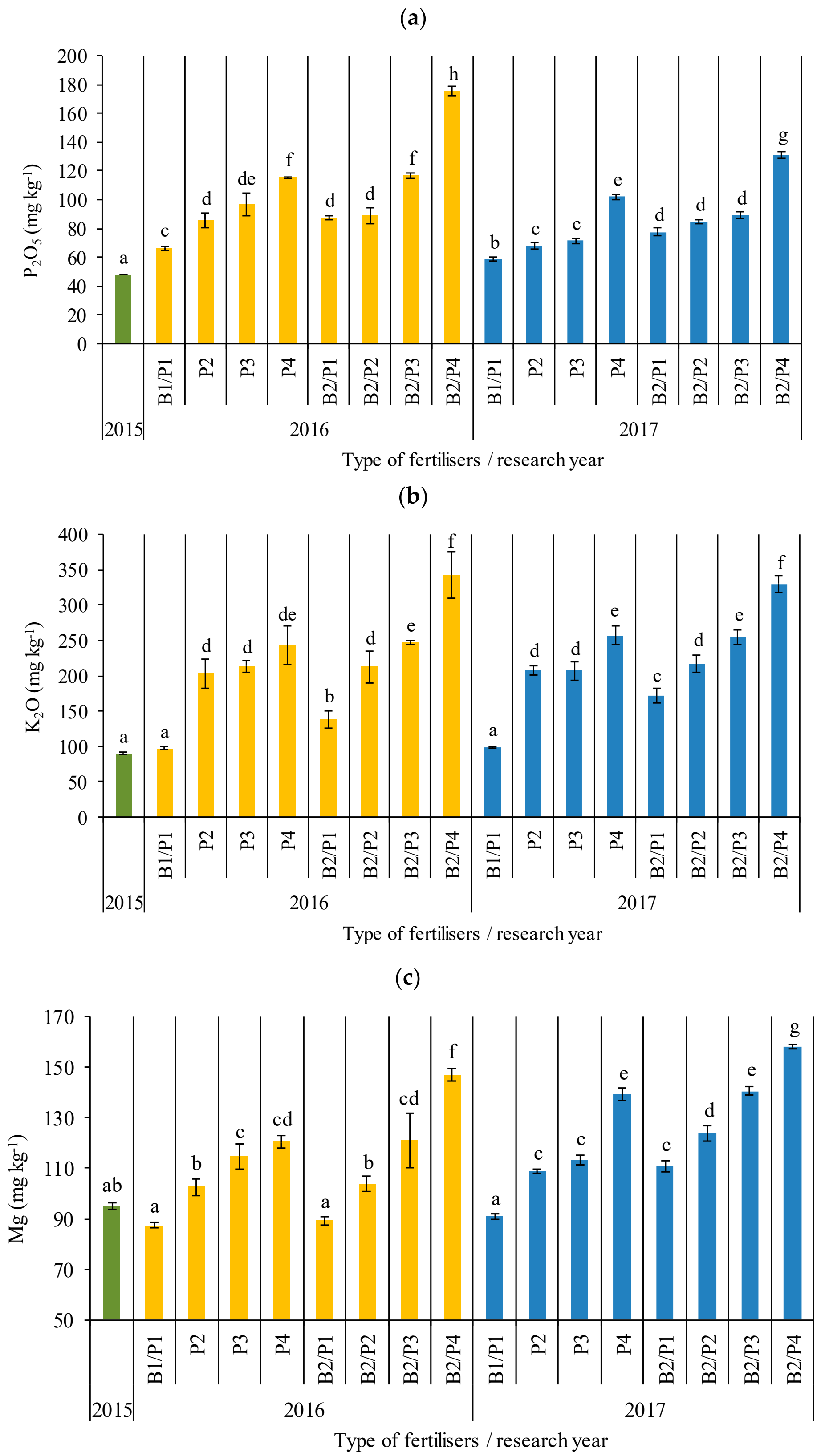


Figure 2. Contents of absorbable forms of phosphorus P_2O_5 (**a**), potassium K_2O (**b**) and magnesium Mg (**c**) in the soil prior to the experiment (2015) as well as following the first and the second year of cultivation, in relation to the type of fertiliser applied. The mean values marked with the same letter do not differ significantly at a level of $\alpha \leq 0.05$ based on the results of the Bonferroni test.

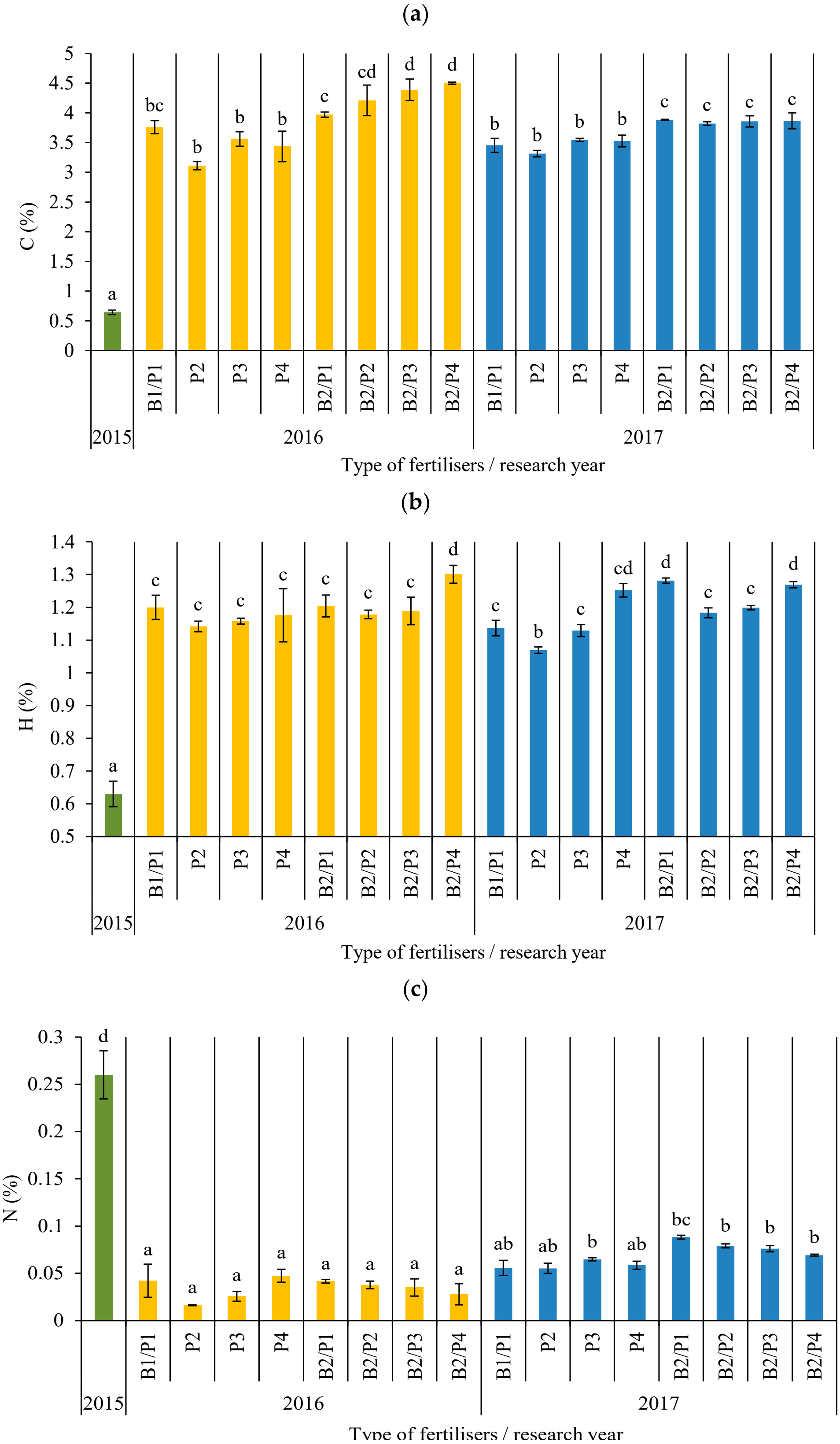


Figure 3. Contents of carbon (**a**), hydrogen (**b**) and nitrogen (**c**) in the soil prior to the experiment (2015) as well as following the first and the second year of cultivation in relation to the fertilisers applied. The mean values marked with the same letter do not differ significantly at a level of α ≤ 0.05 based on the results of the Bonferroni test.

Prior to the experiment, the hydrogen content in the soil amounted to 0.63%, and after the first year of the experiment it increased to 1.2% (control sample). In the subsequent year (2017) there was an insignificant decrease in hydrogen content, to 1.14%. After one year of the experiment, it was found that only the combination of biochar with the highest dose of ash produced a statistically significant increase of soil hydrogen, to 1.3%. At the end of the second year, small differences were observed in this parameter; the contents of hydrogen were in the range of 1.07%–1.28%. Hydrogen along with carbon and oxygen are the major constituents of soil organic matter.

Before the experiment was initiated, the contents of nitrogen in the soil samples amounted to 0.26%. At the end of the first and the second years there was a decrease in the content of this element in the control sample, to 0.04% and 0.06%, respectively. There were statistically significant differences in nitrogen concentrations in the soils amended with all the types of fertilisers and in the control sample, compared to the values identified prior to the experiment. At the end of the first year the content of nitrogen in the soil was in the range of 0.02%–0.05%, and at the end of the second year 0.06%–0.09%.

Table 6 lists the data related to the total contents of selected elements in the soil prior to the experiment and at the end of the first and the second years of cultivation in relation to the fertilisers applied. The highest content of the relevant macro-elements (total calcium, sodium and sulphur) after the first and second years of the experiment was found in the soil amended with a combination of biochar and ash added at the rates of 4.5 t ha^{-1} and 3.0 t ha^{-1}. The findings showed the greatest increase in the total content of these macro-elements in soil samples collected after the first and the second year of basket willow growth when compared to the soil samples collected prior to the experiment. The maximum increase in 2016 and 2017 amounted to 47% and 98%, respectively. The lowest total contents of Ca, Na and S in 2016 and 2017 were identified in the soil amended with ash at the rates of 4.5 t ha^{-1} and 3.0 t ha^{-1}.

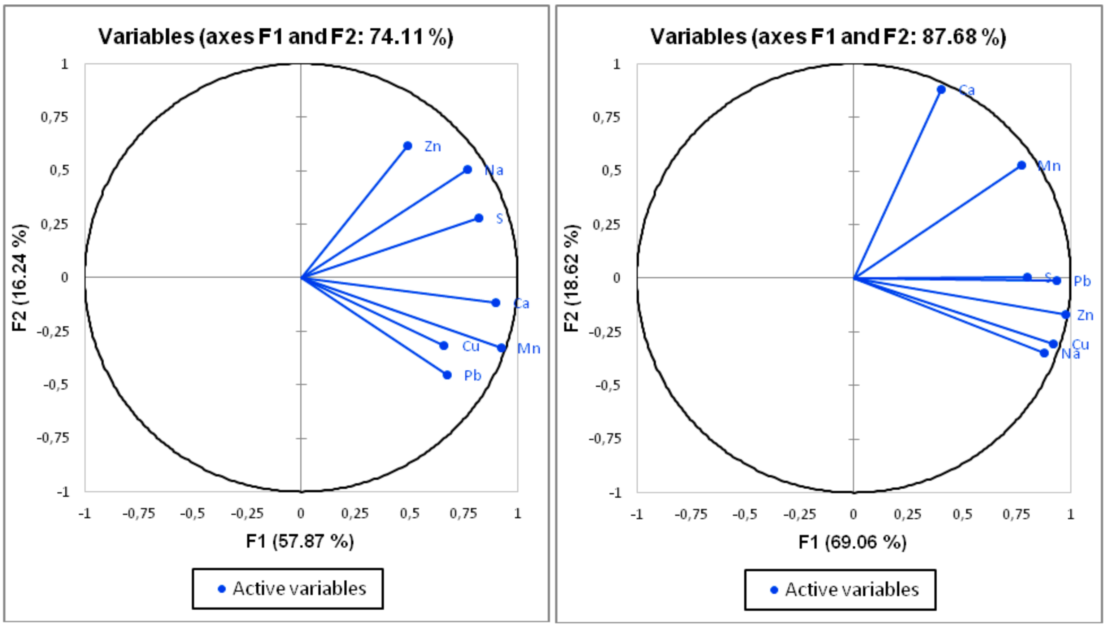
The highest overall contents of the relevant micro-elements after the first and the second years of the experiment were observed in the soil samples from the plots amended with biochar and ash at the rates of 4.5 t ha^{-1} and 3.0 t ha^{-1}, and with ash alone at the rate of 4.5 t ha^{-1}. Following the application of these treatments to the basket willow cultivars, at the end of the first and the second years the total contents of the micro-elements decreased by 10%, 13% and 12%, respectively, relative to the values identified in the soil samples collected prior to the experiment. After the first and the second year, the lowest contents of the micro-elements were found in the soils amended with biochar alone, and with a combination of biochar and ash added at the rate of 1.5 t ha^{-1}. Analysis of the soil samples collected at the start, and following the first and the second years of the experiment failed to identify any arsenic, cadmium or nickel content: values were below the detection limit (0.01 mg kg^{-1}) of the analytical method applied. The content of lead differed slightly, depending on the fertiliser treatment and the year of the experiment, however the respective values never exceeded the levels acceptable on farmland.

Table 6. Contents of selected macro- and micro-elements and heavy metals in the soil prior to the experiment as well as following the first and second years of cultivation, in relation to the fertilisers applied.

Year	Fertilisers Applied	Macro- and Microelements									
		As	Ca	Cd	Cu	Mn	Na	Ni	Pb	S	Zn
		mg kg^{-1}									
		x ± SD									
2015		<0.01	2300.00 ^{b} ± 18.78	<0.01	20.00 ^{a} ± 0.41	624.25 ^{d} ± 4.65	174.75 ^{f} ± 1.50	<0.01	12.40 ^{a} ± 0.41	112.97 ^{a} ± 0.87	50.03 ^{d} ± 2.41
2016	B1/P1	<0.01	2794.63 ^{e} ± 266.27	<0.01	47.43 ^{d} ± 2.89	495.29 ^{b} ± 8.79	17.08 ^{a} ± 9.42	<0.01	15.05 ^{c} ± 0.29	161.72 ^{b} ± 11.31	19.60 ^{a} ± 0.05
	P2	<0.01	2625.47 ^{de} ± 48.51	<0.01	53.47 ^{e} ± 1.00	481.76 ^{b} ± 1.91	89.75 ^{c} ± 36.35	<0.01	13.97 ^{b} ± 0.18	151.19 ^{b} ± 13.66	47.19 ^{d} ± 0.64
	P3	<0.01	2660.68 ^{de} ± 124.12	<0.01	57.83 ^{f} ± 0.33	495.60 ^{b} ± 10.04	98.11 ^{c} ± 41.50	<0.01	14.33 ^{b} ± 0.46	167.72 ^{b} ± 25.44	26.74 ^{b} ± 0.94
	P4	<0.01	2435.24 ^{c} ± 86.36	<0.01	47.67 ^{d} ± 0.62	498.99 ^{b} ± 2.12	13.98 ^{a} ± 4.19	<0.01	15.67 ^{c} ± 0.61	156.95 ^{b} ± 25.53	49.31 ^{d} ± 1.48
	B2/P1	<0.01	2595.98 ^{d} ± 195.27	<0.01	31.02 ^{b} ± 1.87	481.06 ^{b} ± 7.33	86.43 ^{c} ± 15.30	<0.01	14.15 ^{b} ± 0.58	188.72 ^{c} ± 13.63	47.07 ^{d} ± 3.34
	B2/P2	<0.01	2791.68 ^{e} ± 243.24	<0.01	55.11 ^{ef} ± 0.52	495.38 ^{b} ± 11.80	82.34 ^{c} ± 2.30	<0.01	14.76 ^{b} ± 0.46	203.08 ^{d} ± 12.17	48.12 ^{d} ± 2.51
	B2/P3	<0.01	3143.24 ^{f} ± 75.75	<0.01	57.85 ^{f} ± 0.97	512.20 ^{c} ± 2.06	108.07 ^{d} ± 31.87	<0.01	15.00 ^{bc} ± 0.37	203.91 ^{d} ± 1.30	51.33 ^{d} ± 1.26
	B2/P4	<0.01	3427.55 ^{g} ± 51.58	<0.01	62.35 ^{g} ± 0.26	536.15 ^{c} ± 1.47	162.76 ^{e} ± 6.36	<0.01	16.15 ^{c} ± 0.50	223.59 ^{e} ± 4.34	56.37 ^{d} ± 2.15
2017	B1/P1	<0.01	2841.94 ^{e} ± 199.99	<0.01	45.82 ^{c} ± 0.40	445.93 ^{a} ± 10.30	45.97 ^{b} ± 3.43	<0.01	13.48 ^{b} ± 0.52	191.27 ^{c} ± 4.86	26.69 ^{b} ± 0.34
	P2	<0.01	2538.70 ^{d} ± 61.48	<0.01	43.73 ^{c} ± 2.15	473.94 ^{a} ± 8.73	89.37 ^{c} ± 5.10	<0.01	13.83 ^{b} ± 0.18	167.01 ^{b} ± 3.46	28.06 ^{b} ± 0.40
	P3	<0.01	2165.54 ^{a} ± 62.79	<0.01	43.04 ^{c} ± 0.60	478.94 ^{a} ± 8.37	41.63 ^{b} ± 19.56	<0.01	14.65 ^{b} ± 0.17	182.08 ^{c} ± 1.59	27.36 ^{b} ± 0.14
	P4	<0.01	3042.59 ^{ef} ± 276.93	<0.01	61.44 ^{g} ± 1.69	528.60 ^{c} ± 10.19	163.20 ^{e} ± 5.68	<0.01	16.36 ^{c} ± 0.84	196.98 ^{cd} ± 13.23	33.82 ^{bc} ± 2.11
	B2/P1	<0.01	2252.37 ^{b} ± 94.08	<0.01	50.70 ^{e} ± 1.62	475.83 ^{a} ± 6.83	87.55 ^{c} ± 31.15	<0.01	14.34 ^{b} ± 0.21	172.23 ^{bc} ± 3.78	28.44 ^{b} ± 0.56
	B2/P2	<0.01	2162.06 ^{a} ± 21.15	<0.01	44.84 ^{c} ± 0.99	468.23 ^{a} ± 1.73	47.90 ^{b} ± 8.19	<0.01	14.51 ^{b} ± 0.34	168.57 ^{b} ± 6.32	27.22 ^{b} ± 0.45
	B2/P3	<0.01	5132.77 ^{h} ± 131.93	<0.01	43.62 ^{c} ± 0.41	540.16 ^{c} ± 8.48	57.19 ^{b} ± 40.59	<0.01	14.93 ^{b} ± 0.09	183.72 ^{c} ± 1.27	28.85 ^{b} ± 1.18
	B2/P4	<0.01	3217.95 ^{f} ± 32.24	<0.01	60.92 ^{g} ± 1.34	515.14 ^{c} ± 5.74	170.08 ^{e} ± 2.50	<0.01	16.65 ^{c} ± 0.21	205.54 ^{d} ± 1.67	35.73 ^{c} ± 0.70

x means mean, SD means standard deviation. The mean values marked with the same letter do not differ significantly at a level of $\alpha \leq 0.05$ based on the result of the Bonferroni test.

The application of the multidimensional statistical method PCA allowed the determination of elements groups with similar features. Principal component analysis allowed a considerable reduction in a number of variables and also indicated the impact of primary variables on principal components. PCA of the variables (elements) for the soil after the first and the second year of the basket willow cultivation identified two factors describing the level of variability in the group, with the following values in the first year: Factor 1 representing 57.9% and Factor 2 representing 16.2%; and in the second year: Factor 1 representing 69.1% and Factor 2 representing 18.6%. The scree plot and the Kaiser criterion were applied to select the number of principal components. Factor 1 for the first year comprised the variables of calcium, copper, manganese, sodium, lead, and sulphur and for the second year: copper, manganese, sodium, lead, sulphur and zinc. Factor 2 was characterised by the variables of zinc (the first year) and calcium (the second year). In the first year of the study it was found that Factor 1 was most closely related to the variables Ca and Mn, and Factor 2 was linked to the variable Zn. On the other hand, in the second year of the study the findings showed that Factor 1 was mainly related to the variables Cu, Pb, and Zn, and Factor 2 as most closely linked to the variable Ca. Principal component analysis allowed to determine the correlations between the analysed variables. Additionally, it was noted that these correlations differed according on the year of the study. Projections of the variables in a factorial plane are shown in Figure 4.



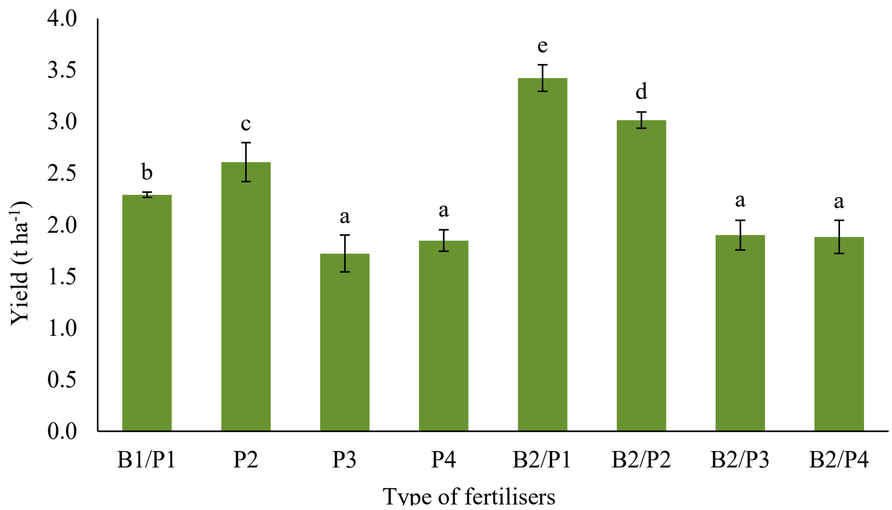
(**a**) (**b**)

Figure 4. Graph presenting variables in a system of two initial factorial axes for soil at the end of the first (**a**) and second (**b**) year of cultivation.

3.3. Basket Willow Biomass

Figure 5 shows the effects of the fertilisers on the yield of basket willow biomass at the end of the first and the second year of the experiment. Mean yield of biomass in the control condition (no fertiliser) amounted to 2.29 t ha^{-1} DM. The highest values of this parameter, i.e., 2.61; 3.42; and 3.01 t ha^{-1} were identified, respectively, in the crops fertilised with ash at a rate of 1.5 t ha^{-1}, with biochar and with a combination of biochar and ash, added at a rate of 1.5 t ha^{-1}. The highest yield of dry plant matter in 2016 was achieved by introducing biochar as an amendment. Fertilisation with ash, doses of 3.0 and 4.5 t ha^{-1}, and with ash combined with biochar resulted in the yield of 1.72; 1.85; 1.90 and 1.88 t ha^{-1} d.m., respectively.

(**a**)



(**b**)

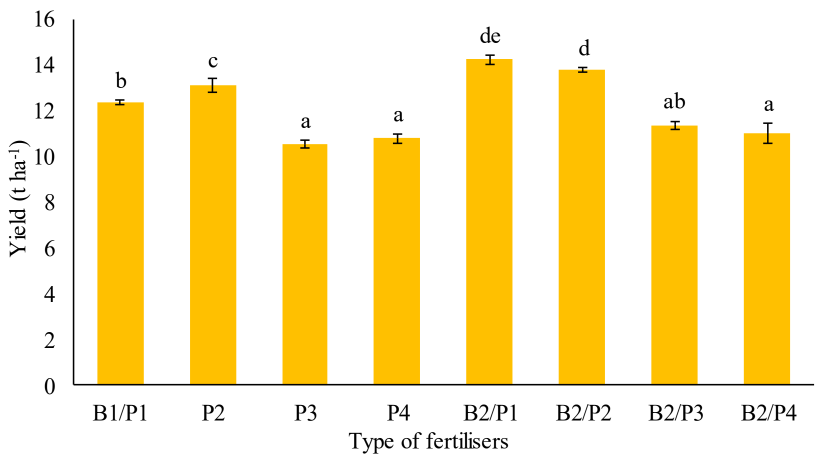
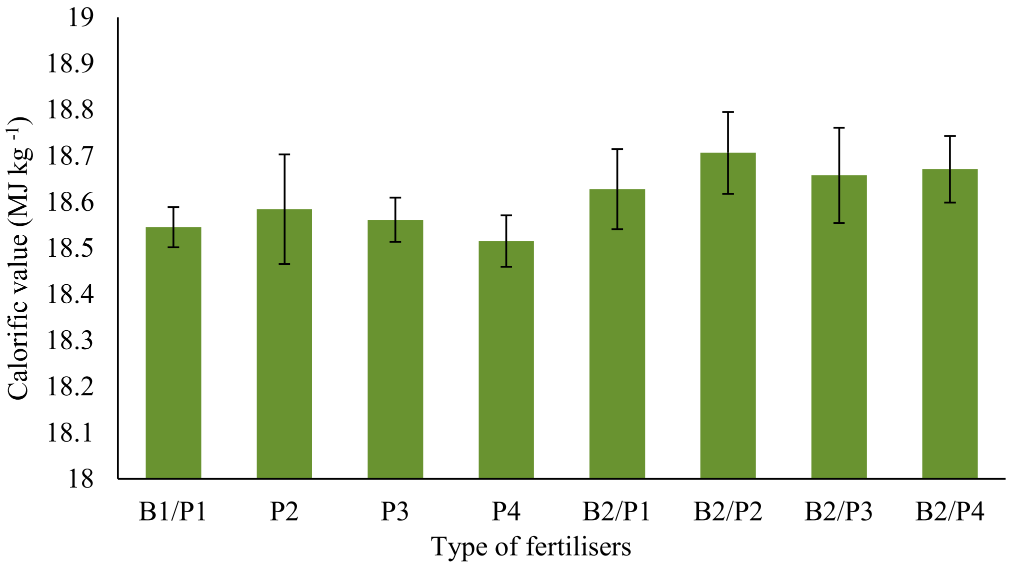


Figure 5. Yield of basket willow at the end of the first (**a**) and second (**b**) year of cultivation in relation to the fertiliser applied. The mean values marked with the same letter do not differ significantly at a level of $\alpha \leq 0.05$ based on the results of the Bonferroni test.

At the end of the second year of growth of basket willow, the mean yield of biomass in the control group amounted to 12.36 t ha^{-1} DM. As in the previous year, the highest mean yield of dry plant matter amounting to 13.07, 14.2, and 13.79 t ha^{-1} was identified, respectively, in the plots fertilised with the lowest dose of ash, with biochar alone, and with a combination of biochar and ash at a dose of 1.5 t ha^{-1}. The highest yield of dry plant matter in 2017 was identified in the plots treated with biochar alone prior to the experiment. The 3.0 and 4.5 t ha^{-1} doses of ash fertiliser and combinations of ash and biochar negatively impacted the crop yield and, compared to the control condition, there was, respectively, a decrease in the mean yield of dry plant matter by 1.86, 1.57, 1.00 and 1.36 t ha^{-1}.

Figure 6 presents the effects of the amendments applied on the calorific value of willow biomass at the end of the first and the second year of the study. The calorific value of the biomass, after the first year of cultivation, was in the range of 18.52–18.71 MJ kg^{-1} DM, and after the second year amounted to 18.62–18.74 MJ kg^{-1} DM. No statistically significant differences were found between these values. The soil amendments applied did not produce changes in the relevant parameter.

(**a**)



(**b**)

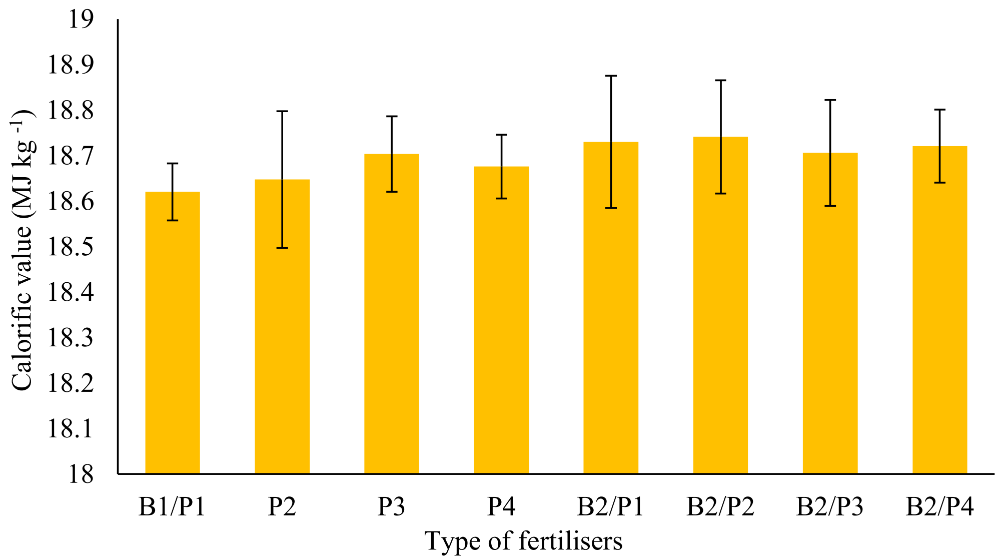
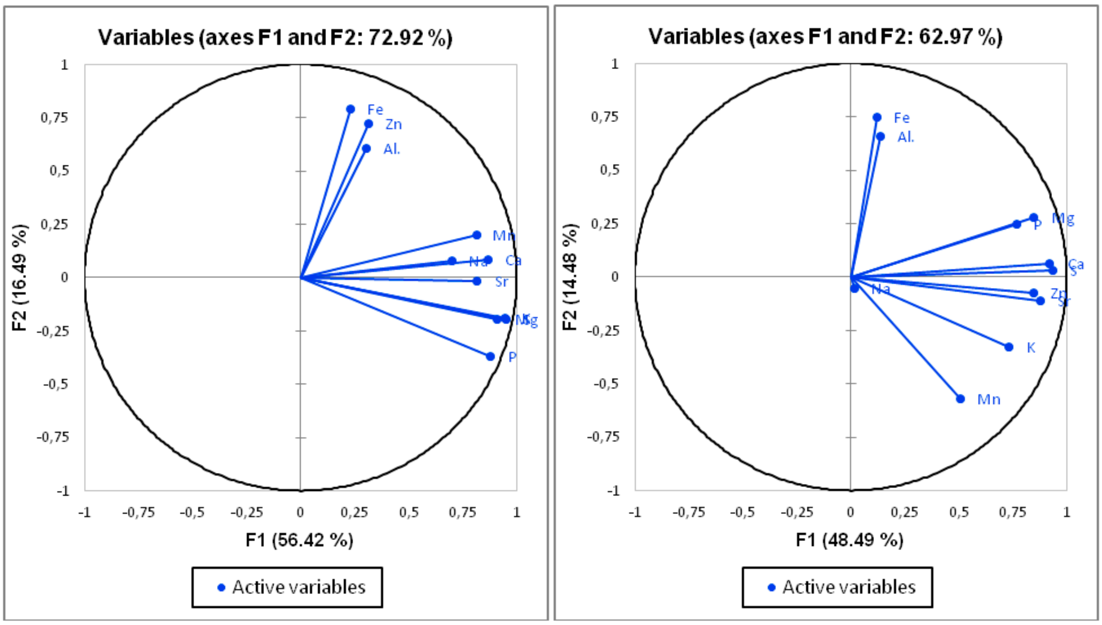


Figure 6. Calorific value of basket willow at the end of the first (**a**) and the second (**b**) year of cultivation, in relation to the fertiliser applied.

Table 7 presents the total contents of the macro-elements analysed in the basket willow biomass in relation to the type of fertiliser applied, and the year of the experiment. At the end of both the first and the second years of the experiment, the greatest increase in the total contents of the macro-elements was identified in the plant biomass from plots fertilised with a combination of biochar and ash at a rate of 1.5 t ha $^{-1}$ and ash alone added at a rate of 4.5 t ha^{-1}. There was a 3% and 9% increase in this parameter, respectively when compared to the control condition. The lowest total contents of these elements, in, respectively, 2016 and 2017, were identified in the case of fertilising with ash (3.0 t ha^{-1}) and a combination of biochar and ash applied at the highest rate. Out of all the ions analysed, calcium was found in the highest concentrations in the basket willow biomass both after the first and second years of cultivation. There were fluctuations in the contents of this element depending on the combinations of the agents used in the experiment; however, not all of the differences were statistically significant.

Analysis of the total contents of the selected macro-elements shows that aboveground parts of basket willow contained the lowest amounts of sodium and iron. The fertilising agents applied did not produce significant changes in the contents of these elements in the biomass at the end of the first and second years of cultivation, compared to the control samples. Table 8 shows the total contents of the selected micro-elements and heavy metals in basket willow biomass, in relation to the type of fertiliser applied and the year of the experiment. The findings show that the aboveground parts of the plants analysed contained manganese, strontium, zinc and aluminium, after both the first and the second year of cultivation. However, very low concentrations of these elements were identified, and there were no statistically significant disparities between the experimental plots. As an exception, the biomass obtained at the end of the first year of the study from the plots treated with fertilisers was found with significantly lower concentrations of aluminium, compared to the control sample. Plant biomass obtained at the end of the second year had lower concentrations of aluminium, and there were no differences in the contents relative to the types of fertilisers applied. It was found that the plant samples subjected to the tests contained no arsenic, cadmium, chromium, copper, molybdenum, nickel or lead at the end of the first and the second year of the experiment values were below the detection limit (0.01 mg kg^{-1}) of the analytical method applied.

Principal component analysis (PCA) of the variables (elements) for the basket willow biomass after the first and the second years of cultivation identified two factors describing the level of variability in the group, with the following values in the first year: Factor 1 representing 56.4% and Factor 2 representing 16.4%; and in the second year: Factor 1 representing 48.5% and Factor 2 representing 14.5%. The scree plot and the Kaiser criterion were applied to select the number of principal components. Factor 1 for the first year comprised the variables of calcium, potassium, magnesium, manganese, sodium, phosphorus, sulphur and strontium and for the second year: calcium, potassium, magnesium, phosphorus, sulphur, strontium and zinc. Factor 2 was characterised by the variables of aluminium, iron and zinc (first year) and aluminium, iron, and manganese (second year). In the first year of the study it was found that Factor 1 was most closely related to the variables K, Mg and S, and Factor 2 was linked to the variables of Fe and Zn. On the other hand, in the second year of the study the findings showed that Factor 1 was mainly related to the variables Ca and S, and Factor 2 was most closely linked to the variables of Al and Fe. Projections of the variables in a factorial plane are shown in Figure 7.



(a) (b)

Figure 7. Graph presenting variables in a system of two initial factorial axes for basket willow biomass at the end of the first (**a**) and second (**b**) years of cultivation.

Table 7. Contents of selected macro-elements in basket willow biomass at the end of the first and the second years of cultivation in relation to the fertiliser applied.

Year	Fertilisers Applied	Macroelements						
		Ca	Fe	K	Mg	Na	P	S
		mg kg^{-1}						
		x ± SD						
2016	B1/P1	5.14 ^{c} ± 0.15	0.12 ^{a} ± 0.04	4.26 ^{c} ± 0.19	0.95 ^{ab} ± 0.04	0.06 ^{a} ± 0.01	1.15 ^{a} ± 0.07	0.87 ^{b} ± 0.04
	P2	4.59 ^{b} ± 0.09	0.34 ^{a} ± 0.15	3.72 ^{ab} ± 0.13	0.87 ^{a} ± 0.03	0.05 ^{a} ± 0.01	1.06 ^{a} ± 0.04	0.77 ^{a} ± 0.02
	P3	4.31 ^{a} ± 0.10	0.08 ^{a} ± 0.03	3.47 ^{a} ± 0.10	0.81 ^{a} ± 0.07	0.05 ^{a} ± 0.01	1.03 ^{a} ± 0.08	0.69 ^{a} ± 0.10
	P4	5.10 ^{c} ± 0.09	0.26 ^{a} ± 0.14	3.76 ^{ab} ± 0.09	0.93 ^{ab} ± 0.04	0.06 ^{a} ± 0.01	1.11 ^{a} ± 0.04	0.76 ^{a} ± 0.06
	B2/P1	4.54 ^{b} ± 0.06	0.07 ^{a} ± 0.03	3.71 ^{ab} ± 0.10	0.86 ^{a} ± 0.05	0.05 ^{a} ± 0.00	1.11 ^{a} ± 0.03	0.78 ^{a} ± 0.01
	B2/P2	5.35 ^{c} ± 0.12	0.08 ^{a} ± 0.05	4.22 ^{c} ± 0.23	1.03 ^{b} ± 0.04	0.06 ^{a} ± 0.01	1.28 ^{b} ± 0.02	0.91 ^{b} ± 0.09
	B2/P3	4.77 ^{b} ± 0.15	0.12 ^{a} ± 0.05	3.91 ^{b} ± 0.09	0.91 ^{a} ± 0.08	0.05 ^{a} ± 0.01	1.16 ^{a} ± 0.05	0.81 ^{ab} ± 0.06
	B2/P4	4.18 ^{a} ± 0.11	0.08 ^{a} ± 0.04	3.56 ^{a} ± 0.12	0.85 ^{a} ± 0.10	0.05 ^{a} ± 0.01	1.08 ^{a} ± 0.10	0.75 ^{a} ± 0.05
2017	B1/P1	1.06 ^{a} ± 0.12	0.04 ^{a} ± 0.01	5.59 ^{c} ± 0.12	0.31 ^{a} ± 0.03	0.09 ^{a} ± 0.00	1.13 ^{c} ± 0.09	0.38 ^{ab} ± 0.01
	P2	1.13 ^{a} ± 0.15	0.06 ^{a} ± 0.02	4.90 ^{b} ± 0.07	0.34 ^{b} ± 0.06	0.08 ^{a} ± 0.00	0.97 ^{b} ± 0.07	0.34 ^{a} ± 0.02
	P3	1.60 ^{c} ± 0.06	0.06 ^{a} ± 0.01	5.37 ^{c} ± 0.09	0.37 ^{b} ± 0.04	0.09 ^{a} ± 0.01	1.25 ^{d} ± 0.07	0.47 ^{c} ± 0.02
	P4	1.26 ^{a} ± 0.08	0.05 ^{a} ± 0.02	4.58 ^{a} ± 0.12	0.36 ^{b} ± 0.01	0.09 ^{a} ± 0.01	1.06 ^{c} ± 0.04	0.37 ^{ab} ± 0.02
	B2/P1	1.17 ^{a} ± 0.12	0.05 ^{a} ± 0.02	4.74 ^{b} ± 0.10	0.28 ^{a} ± 0.03	0.08 ^{a} ± 0.01	0.95 ^{b} ± 0.01	0.32 ^{a} ± 0.01
	B2/P2	1.22 ^{a} ± 0.19	0.05 ^{a} ± 0.03	4.34 ^{a} ± 0.08	0.29 ^{a} ± 0.05	0.07 ^{a} ± 0.01	0.81 ^{a} ± 0.09	0.33 ^{a} ± 0.03
	B2/P3	1.15 ^{a} ± 0.03	0.04 ^{a} ± 0.02	4.78 ^{b} ± 0.11	0.39 ^{b} ± 0.10	0.07 ^{a} ± 0.01	0.79 ^{a} ± 0.08	0.39 ^{ab} ± 0.03
	B2/P4	1.44 ^{b} ± 0.07	0.05 ^{a} ± 0.01	4.66 ^{a} ± 0.12	0.40 ^{b} ± 0.05	0.09 ^{a} ± 0.00	1.09 ^{c} ± 0.07	0.42 ^{b} ± 0.02

x means mean, SD means standard deviation. The mean values marked with the same letter do not differ significantly at a level of $\alpha \le 0.05$ based on the results of the Bonferroni test.

Table 8. Contents of selected micro-elements and heavy metals in basket willow biomass at the end of the first and second years of cultivation in relation to the fertilisers applied.

Year	Fertilisers Applied	Microelements										
		Al	As	Cd	Cr	Cu	Mo	Ni	Pb	Mn	Sr	Zn
		mg kg^{-1}										
		x ± SD										
2016	B1/P1	0.11 ^{b} ± 0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.01	0.03 ^{a} ± 0.01	0.07 ^{a} ± 0.02
	P2	0.08 ^{ab} ± 0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05 ^{a} ± 0.01	0.03 ^{a} ± 0.01	0.07 ^{a} ± 0.02
	P3	0.04 ^{a} ± 0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05 ^{a} ± 0.01	0.03 ^{a} ± 0.01	0.09 ^{a} ± 0.03
	P4	0.06 ^{a} ± 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.01	0.03 ^{a} ± 0.00	0.11 ^{a} ± 0.04
	B2/P1	0.04 ^{a} ± 0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05 ^{a} ± 0.00	0.03 ^{a} ± 0.00	0.05 ^{a} ± 0.02
	B2/P2	0.04 ^{a} ± 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.01	0.04 ^{a} ± 0.00	0.05 ^{a} ± 0.02
	B2/P3	0.04 ^{a} ± 0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05 ^{a} ± 0.01	0.03 ^{a} ± 0.00	0.04 ^{a} ± 0.01
	B2/P4	0.04 ^{a} ± 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05 ^{a} ± 0.01	0.03 ^{a} ± 0.01	0.04 ^{a} ± 0.02
2017	B1/P1	0.01 ^{a} ± 0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07 ^{a} ± 0.01	0.02 ^{a} ± 0.00	0.06 ^{a} ± 0.00
	P2	0.01 ^{a} ± 0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.00	0.02 ^{a} ± 0.00	0.06 ^{a} ± 0.00
	P3	0.01 ^{a} ± 0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.00	0.02 ^{a} ± 0.00	0.06 ^{a} ± 0.00
	P4	0.01 ^{a} ± 0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07 ^{a} ± 0.00	0.02 ^{a} ± 0.00	0.07 ^{a} ± 0.00
	B2/P1	0.01 ^{a} ± 0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.00	0.02 ^{a} ± 0.00	0.07 ^{a} ± 0.01
	B2/P2	0.01 ^{a} ± 0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.01	0.02 ^{a} ± 0.00	0.06 ^{a} ± 0.01
	B2/P3	0.01 ^{a} ± 0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.01	0.02 ^{a} ± 0.00	0.06 ^{a} ± 0.01
	B2/P4	0.01 ^{a}±0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06 ^{a} ± 0.00	0.02 ^{a} ± 0.00	0.06 ^{a} ± 0.00

x means mean, SD means standard deviation. The mean values marked with the same letter do not differ significantly at a level of $\alpha \leq 0.05$ based on the results of the Bonferroni test.

4. Discussion

Research into the use of biochar and biomass ash from energy crops unquestionably supports endeavours related to conservation of the natural environment, in particular taking into account phytoremediation and the utilitarian dimension of the sustainable energy economy. The use of biochar and biomass ash as a soil amendment may strengthen the ecological aspect of energy engineering in agriculture.

Prior to the field experiment, the soil was characterised by an acid reaction with pH in 1 M KCl —4.98. Notably, the soil reaction determines the effectiveness of numerous processes occurring in soils, and as a result affects, directly or indirectly, the transformation of matter and absorbability of nutrients, as well as the development of living organisms, including the yield of crops [30]. In acidic soils certain plant nutrients, e.g., molybdenum, boron and phosphorus, are transformed into forms which are difficult to absorb. In such soils the quantity of organic matter decreases, while the activity of heavy metals, such as lead, increases, along with their availability to plants. Soil acidity is most commonly neutralised by liming, carried out on a regular basis [47,48]. Fertilisation of acidic soils with biochar and biomass ash may be an alternative to liming. Ash from plant biomass is characterised by an alkaline reaction and contains biogenic elements necessary for plant growth, as a result it can be used as a fertiliser in crop farming as a way to control the acid-base balance and supply macro- and micro-elements [16,17,49–54]. The ability to neutralise acidity results from high concentrations of calcium carbonate and magnesium in ash [55–57]. Numerous authors have shown the alkalising properties of ash [19,57,58] and biochar [59–61]. Kraska et al. reported that 12 months after the soil was amended with biochar, at a rate of 30 t ha^{-1}, the soil pH increased by nearly one unit [62]. According to Antonkiewicz and Park et al., the most effective soil acidity control is achieved with doses of ash in the range of 10–20 t ha^{-1} [63,64], while Właśniewski reports the most effective dose as 67.3 t ha^{-1} [65]. However, such high doses are linked with a risk of introducing excessive amounts of nutrients and heavy metals into the soils [54,66]. It was determined the soil in which the experiment was carried out required alkalisation (pH 4.98). The fertilising agents, applied at varied rates and in different combinations, led to an increase in soil pH in the range of 0.46–1.05 after the first year, and 0.04–1.05 after the second year of basket willow cultivation, by reference to the control sample. These findings are consistent with the results obtained e.g., by Osaji K. et al., who suggested that each dose of biochar added to acidic soil would produce positive effects in pH regulation [67].

Analysis of the results obtained in the field experiment showed that the addition of biochar and ash at the rate of 4.5 t ha^{-1} resulted in the greatest increase in the contents of absorbable forms of phosphorus, potassium and magnesium in the soil. At the end of the first year of the experiment, the contents of these elements increased by 165%, 253% and 68%, respectively, compared to the control sample. After the second year of basket willow growth the findings relating to the same type of fertiliser showed a slight increase in magnesium concentration and a decrease in the contents of phosphorus and potassium, relative to the previous year. Plant biomass ash contains biogenic elements indispensable for the normal growth of crops, and therefore by adding this type of fertiliser to the soil it is possible to improve the concentrations of micro- and macro-elements [68,69]. This type of ash is found with the highest contents of potassium and calcium. Accordingly, plant biomass ash may contain up to approximately 40% K_2O, and over 60% CaO [16,17]. Meller and Bilenda emphasise that ash from straw covers the demand for potassium in full, and as a result this is a good potassium fertiliser [53]. In their study Kraska et al. found that fertilising soil with wheat straw biochar at a rate of 30 t ha^{-1} resulted in an increased concentration of potassium in the soil after 24 months, reaching the level of 145.3 mg kg^{-1} [62]. Magnesium is another component of ash which is essential for the normal growth of plants. Its total content in ash may exceed 5% [16,17,57]. Piekarczyk et al., in a laboratory experiment, added ash from spring barley straw to soil at a rate of 2.0 t ha^{-1} and demonstrated an increase of over 13% in the contents of absorbable magnesium in a soil which initially had a low concentration of this element; moreover a dose of 8 t ha^{-1} led to a 50% increase in the content of this element. It was also shown that subsequent higher doses of this ash to the soil produced an increase in magnesium concentration [14].

The results obtained by the authors of the study show that in the second year of basket willow growth, the levels of potassium and phosphorous in the soil decreased slightly; this may have been caused by greater mobility and susceptibility of these elements to leaching from the soil [70]. Da Silva et al. investigated the effects of biochar of varied origin (rice husk, sorghum silage and sawdust) in the soil properties and yield of common bean. The findings showed increased concentrations of cation exchangers (K, Ca and Mg) and P in the soil [71]. Changes in the accumulation of easily absorbable elements in soils depend e.g., on the quantity of fertiliser used (ash, biochar, or their combinations), the origin of fertilising materials, and their elemental composition, which may vary significantly [68].

In the literature it has been reported that biochar contributes to increased sequestration of organic carbon in soils, which leads to decreased emissions of greenhouse gases into the atmosphere [72]. The biochar used in this field experiment had a high content of organic carbon, at a level of 74.35%. Application of biochar at a rate of 11.5 t ha^{-1} and the use of biochar–ash combinations led to an increase in the contents of free carbon in the soil, even by over 40%, in the two years of the experiment. A similar result was reported by Zhang et al. who found a 44% increase in the content of organic carbon in soil fertilised with biochar from wheat straw, applied at a rate of 20 t ha^{-1} [73]. Furthermore, Haefele et al. observed a 66.5% increase in soil carbon following the application of biochar from rice husk as a fertiliser, added at a rate of 41.3 t ha^{-1} [74]. Introduction of ash into the soil did not result in a significant increase in the contents of free carbon in the soil. The ash applied as a fertiliser was characterised by a low content of organic carbon at a level of 1.22%.

The content of soil nitrogen in the samples from the control plots was 0.02% after the first and 0.07% after the second year of the experiment. As a result of the fertiliser applied, there was only an insignificant and non-uniform increase in the concentration of this element relative to the control sample. Njoku et al. observed a small increase in total nitrogen contained in the soil (by 10% and 11%, respectively) following the application of biochar and wood ash at a rate of 5 t ha^{-1} [75]. The joint use of biochar and ash soil amendment at the highest dose produced the most significant increase in the total cumulative content of calcium, sodium and sulphur at the end of both the first and second years of basket willow growth, relative to the year 2015. The soil in which the experiment was conducted was found to contain no heavy metals, i.e., arsenic, cadmium and nickel, prior to and throughout the duration of the experiment. During the experiment the concentration of lead increased slightly, but the acceptable limits were not exceeded. These findings are consistent with the results reported by Olanders and Steenari who concluded that ash from straw or other types of plant biomass can safely be used because these materials are not toxic [76]. On the other hand, Lu et al. recommend biochar as a soil amendment which allows one to reduce the mobility of heavy metals in soils [77].

The most important parameters describing energy crops include biomass productivity and calorific value. The study investigated the effects of various types of fertiliser treatment using biochar and biomass ash on dry matter yield from basket willow. Compared to the control sample, the greatest increase in dry matter yield from the plants after the first and the second year of the experiment was found in the plots fertilised with biochar (49% and 15%, respectively). Ash fertiliser applied at the rates of 3.0 t ha^{-1} and 4.5 t ha^{-1} as well as combinations of the latter doses with biochar adversely affected the yield of basket willow relative to the control plots. Szczukowski et al. and Jeżowski et al. conducted field experiments and reported that the mean yield of willow, in Poland cultivated in a short-term rotation system, is in the range of 10–15 t ha^{-1} of dry matter [78,79]. The low biomass productivity in the experiment, identified after the first year of growth, is associated with the fact that at that stage the plant is rapidly developing its root system, at the expense of the aboveground parts. Uzoma et al. observed positive effects of cow manure biochar application on maize productivity. Application of the fertiliser at a rate of 15 t ha^{-1} led to a 150% increase in maize grain yield, while a dose of 20 t ha^{-1} led to an increase in yield by 98% [80]. Mbah et al., in a two-year field experiment, assessed the effects of wood biochar on the yield and agronomic parameters of cucumber (*Cucumis sativus* L.). Application of biochar in all the doses examined led to an increase in all of the parameters, i.e., vine length, fruit length, number of fruit and productivity. The largest increase in the parameters was observed when biochar was applied at a rate of 5 t ha^{-1}; in this case the yield was 37% higher than in the control sample [81]. Uzoma et al., Chan et al., and Demeyer et al. demonstrated in their experiments that the addition of biochar to soil favourably affects soil quality, improving the availability of nutrients for plants and consequently leading to enhanced growth and a better yield of the plants [8,80,82]. According to related literature, the beneficial effects are produced by fertilisers applied at rates up to 55 t ha^{-1}; higher doses of biochar do not lead to statistically significant changes in plant productivity [66,72]. Biel et al. conducted a field experiment and showed that application of ash from conifer biomass leads to a statistically significant increase in the dry matter identified in tubers of Jerusalem artichoke. It was found that a higher dose of the biomass ash coincided with a greater increase in dry matter content in the tubers [83]. Cucumber yield was 37% higher when wood ash was added at a rate of 5 t ha^{-1} compared to a 4% increase in cucumber productivity following the application of biochar at the same rate [75]. Saletnik et al. assessed the effects of biochar and ash applied as a soil amendment on the productivity of giant miscanthus and observed an increase in the yield relative to the control sample, in the range of 11%–68% following combined application of biochar (11.5 t ha^{-1}) and biomass ash from energy crops (1.5 t ha^{-1}) [66].

The calorific value of the basket willow biomass obtained ranged from 18.52 to 18.74 MJ kg^{-1} DM. By reference to the control samples, the findings show no statistically significant changes in this parameter following application of the amendments. Likewise, Saletnik et al. also failed to find effects of soil amendment with biochar and ash in the calorific value of giant miscanthus [66]. The current findings related to calorific value correspond to typical results reported for this parameter by other researchers [84,85].

Laboratory analysis of the biomass from basket willow shows mean total contents of the elements taken into account in the following order: Ca > K > P > Mg > S > Fe > Zn > Al > Mn > Na > Sr after the first year, and Ca > K > P > Mg > S > Zn > Mn > Fe > Sr > Na > Al after the second year of the experiment. At the end of the second year the findings showed a decrease in the mean total contents of macro-elements in the biomass of willow leaves and stems, compared to the previous year. The plant biomass collected was characterised by the highest contents of Ca, P, and K. High levels of calcium and potassium in one-year stems of basket willow were also identified by Otepka and Haban [86] in a long-term study of effects produced by wood ash in basket willow growth as well as by Borkowska and Lipiński [87] in a study focusing on the contents of macro- and micro-elements in energy crop biomass.

The laboratory analyses conducted for the current study showed that the biomass of basket willow did not contain toxic elements, i.e., arsenic, cadmium, chromium, and lead. Kalambasa et al. [88] investigated the effects of sewage sludge applied as a soil amendment at various rates in the contents and absorption of heavy metals by basket willow. In most cases, the biomass from the control sample did not differ in the content of lead, copper and nickel from the biomass in the study samples. The contents of cadmium, chromium and zinc tended to be higher in the biomass from the control plots compared to the plots fertilised with sewage sludge. By reference to the biomass from the control plots, higher contents of lead and comparable concentrations of cadmium and zinc were only found in the willow biomass growing in plots fertilised with the highest dose of sewage sludge (200 kg N ha^{-1}). Jiang et al. investigated the effects produced by the application of rice straw biomass to polluted soils. Their assessments of copper and lead concentrations showed that, in soils with biochar added, the contents of Cu decreased by 19.7%–100% and Pb decreased by 18.8%–77.0%, compared to the control soils. Furthermore, application of the biochar led to an increased proportion of Cu, Pb and Cd fractions immobilised in soil [89].

5. Conclusions

The results obtained from the field experiment suggest that biochar and ash from plant biomass can be used as a fertiliser in the cultivation of basket willow (*Salix viminalis* L.). By applying a correctly selected dose of biochar and biomass ash it is possible to improve the chemical characteristics of soil, including its pH, and increase the contents of absorbable forms of macro-elements, and micro-elements, while reducing concentrations of mobile forms of heavy metals such as Pb and Cd. The analyses conducted show that an appropriately defined dose of biochar and biomass ash fertiliser produces an increase in the yield of basket willow (*Salix viminalis* L.). The greatest increase in the yield of plant dry matter may be achieved by the application of biochar at a rate of 11.5 t ha^{-1}. Application of biomass ash at the rate of 3.0 t ha^{-1} or higher results in decreased productivity of basket willow. The biochar used in the experiment produced a wide range of positive effects in the soil properties and plant growth, and therefore it appears to be a better soil amendment than ash. The results obtained confirm that biochar and biomass ash may be a good soil amendments, particularly in soils which are severely damaged and require restoration. The experiment should be continued for a number of years to enable further investigation to be carried out on the soil characteristics and basket willow productivity.

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