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The Effect of Biochar Particle Size on the Leaching of Organic Molecules and Macro- and Microelements

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Abstract: Biochar is a carbon-rich material that has recently received attention due to its increasing agronomical potential. The agricultural utilization of biochar relates to its potential to act in the soil as a soil conditioner; nevertheless, complex information on the direct dependence of biochar's physical properties (texture, particle size) and corresponding leaching and availability of organic molecules (e.g., the polycyclic and heterocyclic organic compounds) and inorganic mineral salts (based on micro- and macroelements) is still inconsistent. Multi-elemental analysis by using inductively coupled plasma atomic emission spectroscopy (ICP-OES) was used to assess the information on the contents and availability of macro- and microelements in studied commercial biochar samples. The results showed a statistically significant indirect relation between an increase in the size fraction of biochar and the content of aqueous-extractable K and Na and the direct relation with the aqueous-extractable Ca, Mg, and P. Compared to the macroelements, the detected contents of aqueous-extractable microelements were almost three orders lower, and the dependence on fraction size was not consistent or statistically significant. In addition, gas chromatography (GC) coupled with mass spectroscopy (MS) was further used to reveal the concentrations of available polycyclic aromatic and heterocyclic compounds in biochar samples. The detected concentrations of these types of organic compounds were far below the certified limits, and a statistically significant indirect correlation with particle size was also observed for all the studied biochar samples. The proposed methodological concept could provide the necessary insights into the description of biochar mineral content and its connection to biochar texture, the physicochemical properties, and the potential of biochar to release nutrients into the soil. These findings could help in the further assessment of biochar as a soil conditioner in modern agriculture.

Keywords: agriculture; biochar; fraction size; mineral and organic content; polyaromatic hydrocarbons; soil conditioner

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1. Introduction

Biochar is a carbon-rich material produced by the thermal transformation of organic biomass in an oxygen-limited atmosphere (pyrolysis). In recent years, research interests related to the potential agronomical utilization of biochar as a soil conditioner have grown in importance. This trend was probably stimulated by early studies of Terra Preta soil of the Amazon—an example of unusually fertile black carbon-rich soil historically formed due to the agricultural practices of ancient farmers. This unique soil has maintained its extraordinary fertility and physicochemical properties over the centuries [1].

The properties of biochar are closely linked to its chemical composition, internal porous structure, and physicochemical properties. These characteristics are related to the origin of the used biomass feedstock materials (woody, non-woody) and to the parameters of pyrolysis (temperature, residence time) and the pre-treatments used before the biomass transformation to biochar [2,3]. The broad variety of driving factors affecting the crucial biochar characteristics results in the high heterogeneity of this unique material [3]. Therefore, in 2012, the European Biochar Certificate was established to create close cooperation

between scientists and biochar producers [4], with the aim of creating an industry standard that would guarantee biochar's properties and minimize both the potential risk of undesirable side effects and the presence of toxic substances.

The promising soil-conditioning effects of biochar are connected with its potential to reduce the release of greenhouse gases [5], to affect nutrient (P, N, Mg, Ca, K) leaching [6], to reduce heavy metal (e.g., As, Cu, Pb, Cr, Cd) mobility [7], to influence the content of soil organic matter, to increase the ion-exchange capacity of soil [8], and to positively affect soil microorganisms [9]. In addition to influencing the chemical and microbiological characteristics of soil, biochar can also influence the physical properties of soil via its direct impact on soil structure, density, porosity, pH, conductivity, and compactness. All these potential soil-conditioning effects of biochar are connected with its mode of action in soil, which is based on (i) action as the sorbent of various inorganic (heavy metals, multivalent ions) and organic molecules (polycyclic aromatic compounds, substituted heterocycles) and ionic compounds as well as on (ii) action as the source of various organic (substituted aliphatic and aromatic moieties originating from decomposed biomass) and mineral molecules and ions (mineral ions—K, Na, Mg, Ca), which can be leached to the surrounding soil [10]. The potential release of molecules to the surrounding soil can even be pronounced in coarse-textured soils with more significant water infiltration rates. Moreover, the studies [11,12] also confirmed the direct relationship between a decrease in the fraction size of biochar particles and the content of total extractable nutrients. Thomas et al. [13] and Akhtar et al. [14] have strengthened the importance of biochar particle size. Smaller biochar particles have a more significant effect on soil sorption capacity—and thus plant growth, especially under salt stress. This effect can be explained by improved soil-biochar contact between particles [10]. There may be an optimal biochar particle size for enhancing plant growth responses as far as large biochar particles may reduce particle mixing and accessible surface area for sorption. On the other hand, very small biochar particles can have reduced effects on soil water holding capacity, and their application can lead to increased soil conductivity and pH [15]. Recent literature presents an optimal biochar particle size in the range of 0.5–1.0 mm [13]. The optimal particle size of biochar is also crucial from the agronomical point of view concerning its application on the field during tillage or when using mechanical spreaders, where, depending on the spreader construction, the optimal particle size can be in the range of 1–5 mm [16]. From the agronomical point of view, inorganic elements acting in the soil as nutrients can be divided according to their importance into macroelements (N, P, K, Na, Ca, Mg) and microelements (Al, Fe, Zn, Mn, Cu, Cr, Ni); macroelements can be further separated into primary (N, P, K) and secondary (Ca, Mg) [17]. Macroelements are often applied in agriculture artificially as plant nutrients in the form of inorganic-based fertilizers, which, besides their positive effects on soil fertility, can lead to an increase in soil salinity and a decrease in the activity of soil microorganisms [18]. Agronomically important are also micronutrients, whose presence in natural soils is in the three orders lower of magnitude (in ppm), compared to macronutrients [19]. Besides the mineral contents, another important group of chemicals, which need to be monitored in biochars having potential use in agriculture, are the polycyclic organic compounds. These toxic substances can be co-generated during biochar production as side products of biomass pyrolysis [20,21]. Probably the most important group of polycyclic aromatic compounds—polyaromatic hydrocarbons (PAHs)—can be further divided according to the molecular weight of individual substances into low molecular weight (LMW) PAHs, containing two to three benzene nuclei, and high molecular (HMW) PAHS, containing four to seven benzene rings in the structure of a molecule. HMW PAHs exhibit many times higher levels of toxicity than LHMW PAHs [21]. Despite the serious toxic effects of these compounds, their mobility is limited, as they are strongly bound to the residual biochar matrix. Hale et al. [22] reported that the bioavailable fraction of PAHs in biochar is approximately 1% of their total content.

According to the above-summarized findings, the fraction size of biochar plays an important role and, together with specific surface area, defines the texture of biochar.

The biochar texture is a producer-dependent parameter playing an important role in the final physicochemical properties of biochar but also in its potential to release various organic and inorganic compounds. The literature provides a detailed discussion on the importance of an appropriate selection of source biomass feedstock [23,24], biomass pre-pyrolysis treatment [25], and pyrolysis conditions [23,26,27] as the important prerequisites driving the final properties of the produced biochar. On the other hand, there is a lack of information on the corresponding effects of particle size on leaching of the particular mineral and organic contents of biochar. This information gap was already pointed out in our previously published research [12], where the minor effects of biochar fraction size and its texture on the main structural features and more significant effects on its physicochemical properties, specific surface area, and the total contents of organic and inorganic constituents were revealed. The attention of the present work was aimed at a further experimental extension of our previously published research [12], and we focused on a specification of the effects of biochar fraction size on total and aqueous-extractable contents of the particular macroelements (Na, Ca, Mg, K, P), microelements (Al, Fe, Zn, Mn, Cu, Cr, Ni), and heavy metals (Cd, Co, As, Pb), which can be present in biochar structure and at certain conditions can be also released. These groups of inorganic salts can positively influence the soil physicochemical properties and support the soil nutrient contents. Therefore, the presence and availability of minerals in the biochar structure were correlated with the physicochemical properties of the studied materials. Moreover, the effect of biochar fraction size on the organic matter content and the availability of organic matter to the surroundings represent the second important parameter addressed by this study. These groups of compounds can positively influence/conditionate the properties of soil as well as its fertility. Among them, there is a specific group of polycyclic organic compounds (substituted PAHs, nitrogen and sulfur heterocycles, and substituted naphthalenes), which, according to the EBC [4], can be co-generated during biochar production and need to be monitored, as they exert toxic effects in the soil. These characteristics of studied fractions of biochar samples and their potential to release minerals and organic molecules were subsequently compared and discussed with the data obtained for biochar samples collected after the termination of the pot cultivation experiment (2 years in total) in selected soil samples with the presence of corn (*Zea mays*) as the model plant. The set of biochar complex characteristics represented by the content and potential availability of mineral nutrients, organic molecules, and polycyclic aromatic compounds and the connection of these characteristics to the corresponding fraction size of biochar (together with its specific surface area) will provide the necessary insights, which could help in further assessment of biochar use in agriculture, where it could serve as a promising soil supplement.

2. Materials and Methods

2.1. Biochar Sieve Analysis

The biochar samples used in the work were commercially produced for use in agriculture as soil conditioners. These samples were purchased from Sonnenerde GmbH (Bio Pflanzenkohle, Riedlingsdorf, Austria) and NovoCarbo GmbH (NovoTerra, Hamburg, Germany), and both possess the European Biochar Certificate (EBC) [4]. The third sample was biochar produced by the company Biouhel.cz s.r.o. (Agrouhel, Zlín, Czech Republic), also for use in agriculture.

Biochar samples used for the cultivation experiments were utilized in the forms obtained from the producers without any further pre-treatment. The samples used for studying the particular effects of fraction size were initially air-dried at 45 °C for 48 h to remove the absorbed moisture (which might have influenced the fractionation of biochar during the sieve analysis). The dried samples were sieved by an AS 2000 Vibratory Sieve Shaker (Retsch GmbH, Haan, Germany) generating the following size fractions—Fraction A (below 0.5 mm), Fraction B (0.5 to 2.0 mm), Fraction C (2.0 to 4.0 mm), and Fraction D (above 4.0 mm). All the producers declared information about the biochar samples, and their fractions are summarized in Table 1. Prior to the instrumental characterization,

the obtained pretreated fractions of biochar were milled using an HK 40 desktop swing mill (H&K Laboratory equipment, Turnov, Czech Republic) in an HKMG6 zirconia oxide grinding vessel.

Table 1. Summary of information about the biochar samples and their prepared fractions.

Label	Fraction	Producer	Feedstock	Pyrolysis Conditions
BCH-S-A	<0.5 mm	Sonnenerde GmbH, Austria	corn and sunflower peels, fruit sludge	20 min, max. 650 °C
BCH-S-B	0.5–2.0 mm			
BCH-S-C	2.0–4.0 mm			
BCH-S-D	>4.0 mm			
BCH-N-A	<0.5 mm	NovoCarbo GmbH, Germany	softwood woodcut	10 min, max. 720 °C
BCH-N-B	0.5–2.0 mm			
BCH-N-C	2.0–4.0 mm			
BCH-N-D	>4.0 mm			
BCH-CZ-A+B	<2.0 mm	Biouhel.cz s.r.o, Czech Republic	corn digestate, wheat straw, grass biomass	20–30 min, 450–470 °C
BCH-CZ-C+D	>2.0 mm			

Visualization of morphology and internal porous structure of individual biochar samples was obtained by SEM (Figure S1 in Supplementary Materials). The specific surface area (SSA) of these fractionated and dried biochar samples was characterized by means of Brunauer-Emmett-Teller (BET) analysis. The SEM and BET analyses are described in more detail in our previously published research [12].

The soil samples used in the work consisted of four different soil types from the Czech Republic (sampled from the upper humous horizon, depth of 30 cm). These samples represent the most abundant soil types in the Czech Republic. The first soil type was regosol (arid sandy soil) located in the area of Hodonin–Panov (48.878° N, 17.132° E), the second soil type was chernozem (arenic soil) located in the area of Zabcice (49.006° N, 16.591° E), the third soil type was cambisol (modal soil) located near Namest nad Oslavou (49.213° N, 16.162° E), and the last soil type was fluvisol (modal brown soil) located in the area of Ivan (49.922° N, 16.561° E).

Calcium chloride dihydrate ($CaCl_2 \cdot 2\ H_2O$) and sodium chloride (NaCl) powders of analytical grade purity were purchased from Penta s.r.o. (Praha, Czech Republic) and used without further purification. In all experiments, demineralized water (ELGA Purelab Classic system, ELGA LabWater, High Wycombe, UK) was used for the preparation of extraction solutions.

2.2. Pot Cultivation Experiment

To be able to discuss the results of laboratory leaching experiments in broader terms, long-term pot cultivation experiments were performed. The individual samples of biochar inside semipermeable bags (4 × 4 cm, 5 g of biochar per bag) prepared from polypropylene textile using an impulse bag sealer were applied directly to soil samples and cultivated under driven conditions with the presence of a model plant—*Zea mays* (corn, one corn plant per pot). The individual pots (13 × 13 × 13 cm, maximal volume 1.5 L) used in the experiments contained 1 kg of soil (dry weight of soil) mixed with perlite (4:1 in volume). Perlite was used to aerate the soil. The application dose of biochar was 20 g per 1 kg of individual used soil (details about the sample labels are presented in Table 2).

Pots were placed into a grow box with controlled light exposure based on the average times of sunrise and sunset in the Czech Republic (6:15–18:30). The corn plants were cultivated in repeated vegetation cycles (3 months vegetation cycle, 5 repeated vegetation cycles) for 24 months (in total). Cyclic irrigation (100 mL per pot) took place 3 times a week using tap water (pH and conductivity monitored). After the termination of the pot cultivation experiment, the bags with biochar were separated from the residual soil samples

and air-dried at 45 °C in an oven. These samples were analyzed by the set of instrumental techniques used for the characterization of the original biochar samples.

Table 2. The description of individual biochar samples used for the cultivation experiments and the corresponding samples obtained after the termination of the cultivation experiment.

Label	Biochar	Sample Description	Soil
BCH-S (NF)	Sonnenerde GmbH, Austria	original, not fractionated	–
BCH-S (2Y_F)		cultivated in soil for 2 years	Fluvisol
BCH-S (2Y_C)			Cambisol
BCH-S (2Y_R)			Regosol
BCH-S (2Y_CH)			Chernozem
BCH-N (NF)	NovoCarbo GmbH, Germany	original, not fractionated	–
BCH-N (2Y_F)		cultivated in soil for 2 years	Fluvisol
BCH-N (2Y_C)			Cambisol
BCH-N (2Y_R)			Regosol
BCH-N (2Y_CH)			Chernozem
BCH-CZ (NF) *	Biouhel.cz s.r.o, Czech Republic	original, not fractionated	–

* not used in the cultivation experiment—results only for the original non-fractionated biochar.

2.3. Elemental Analysis and Thermogravimetry

The total contents of organic matter (W_{ORG}) and inorganic mineral ash (W_{MIN}) in the studied fractions of dried and milled biochar samples were measured by a Q5000 thermogravimetric analyzer (TA Instruments, New Castel, DE, USA). For the analysis, 5 mg of a sample was weighed into a platinum pan. The analysis was performed from ambient temperature to a temperature of 1000 °C (under air atmosphere). The heating rate was 10 °C/min. The composition of basic organic elements (C, O, H, and N) was determined using an EA 3000 CHNS/O analyzer (Euro Vector, Pavia, Italy). The analysis was performed on 0.5–1.0 mg of dried and milled sample, which was weighed in tin capsules and packed and subsequently combusted at 980 °C in the analyzer using oxygen as the combustion gas and helium as the carrier gas. The calibration of C, H, N, and S determination was performed using a sulphanilamide standard sample. The relative oxygen content was calculated from the residual combustible mass by using the data (W_{ORG}) from thermogravimetry.

2.4. Measurement of pH and Conductivity of Aqueous Extract

The pH and conductivity of individual fractions of biochar samples were characterized in their aqueous extracts, which were prepared by dispersing 1 g of individual dried and milled biochar samples in 10 mL of demineralized water. The pH of the extract was measured directly in the suspension after 1 h of shaking. Conductivity was measured on the samples obtained from the pH measurement after their filtration through 0.45 µm syringe filters (nylon membrane). Additionally, the pH of biochar extracts was characterized by using the standard calcium chloride method. The dried and milled fractions of biochar (1 g) were dispersed in 10 mL 0.01 M $CaCl_2$ solution. After 1 h of shaking, pH was measured directly in the suspension.

2.5. ICP–OES Analysis

Multi-elemental analysis of both the aqueous-extractable contents and the total contents of inorganic elements in all studied biochar samples was carried out by means of inductively coupled plasma atomic emission spectroscopy (ICP–OES) using the Horiba Jobin Yvonne Ultima 2 system (Horiba Scientific, Palaiseau, France). The following elements were detected—macroelements (Na, Ca, Mg, K, P), microelements (Al, Fe, Zn, Mn, Cu, Cr, Ni), and heavy metals (Cd, Co, As, Pb)—in both used experimental approaches (Sections 2.5.1 and 2.5.2). The calibration was performed by the method of

standard addition into a blank sample. The setting of the ICP-OES analysis is shown in Table S1 (Supplementary Materials).

2.5.1. Content of Aqueous-Extractable Inorganic Elements

To determine the contents of mobile (aqueous-extractable) elements, individual biochar samples (0.5 g) were dispersed in 10 mL of demineralized water. After 1 h of shaking, the samples were filtered through 0.45 μm syringe filters (nylon membrane). The obtained filtrates were directly analyzed using ICP-OES.

2.5.2. Total Content of Inorganic Elements

The samples for the determination of the total content of inorganic elements were prepared by using microwave digestion. The individual biochar samples (0.1 g) were digested in a mixture of 6 mL of HNO_3 and 1 mL of H_2O_2. The setting of the microwave digestion program is summarized in Table S1 (Supplementary Materials). Digested samples were filtered through 0.45 μm syringe filters (nylon membrane) into a 25 mL volumetric flask and filled to the label with demineralized water.

2.6. GC-MS Analysis

The extraction was performed by means of a pressurized solvent extractor (OnePSE, Applied Separations, Allenton, PA, USA). The biochar samples (1 g) were mixed with Hydromatrix (1:1) and transferred into the SPE extraction vessel. An amount of 10 μL of internal standard (10 ng/μL; deuterated PAHs standard, Absolute Standards Inc., Hamden, CT, USA) was added. Toluene (HPLC gradient grade, Merck/Sigma Aldrich, Praha, Czech Republic) was used as an extraction solvent. The extraction was performed in 3 cycles (3 × 15 min) at 130 °C and 120 bars. At the end of the extraction, the vessel was flushed with toluene and nitrogen. Samples were evaporated under a stream of nitrogen and reconstituted in 1 mL of isooctane. GC–MS analysis was performed using Bruker EVOQ GC–TQ instrument (Bruker, Ettlingen, Germany). Calibration was performed by the internal calibration method (deuterated standards mixture and PAHs mixture 38 components, Absolute Standards Inc). The parameters of GC–MS analysis are summarized in Table S2 (Supplementary Materials).

2.7. Statistical Analysis

The individual experiments and instrumental analyses were performed at least in triplicate, and the data are shown in the form of average values ± SD. The experimental data were processed using Microsoft Excel (Microsoft Office Professional Plus 2019 software package) and Statistica (software version 14.1.0.8, Tibco Software Inc., Santa Clara, CA, USA). The statistical significance of the presented results was determined using the Dean-Dixon Q-test for the identification and rejection of outliers (significance level $\alpha \leq 0.05$). The identification of significant differences in the data was performed using ANOVA and Tukey's test (significance level $\alpha \leq 0.05$). Correlation analysis was based on the evaluation of the Pearson correlation coefficient. The significance of the correlation coefficient was tested at a significance level of 0.05. The data were also further processed using multivariate principal component analysis (PCA) based on the Pearson correlation method to determine the statistically significant parameters responsible for the observed trends in the results.

3. Results and Discussion

The effect of biochar particle size on the crucial characteristics important for its possible agronomical utilization is discussed in the present study from three different aspects. Firstly, the variation in the physicochemical characteristics of biochar (Section 3.1.) is assessed. Secondly, the effect on leaching of mineral contents of biochar (Section 3.2) is investigated. Thirdly, the effect on the availability of polyaromatic organic molecules and substituted heterocyclic compounds (Section 3.3) is also taken into account. To be able to discuss these

agronomically crucial characteristics of biochar consistently in real conditions in the soil, the selected biochar samples were applied to the soil (2 years in total). The obtained results were correlated with data from leaching experiments applied to the individual size fractions of the studied biochar samples. These findings together with previously published data could represent crucial knowledge necessary for the further assessment of biochar as the soil conditioner and help to determine its agronomical potential as well as its optimal form and dosage.

3.1. Physicochemical Characteristics

Previously published results [12] revealed the correlation of biochar particle size and texture with its physicochemical characteristics (pH, conductivity, organic and inorganic contents). A direct relation between biochar particle size fraction and the content of organic matter, organic carbon, and partially organic nitrogen (data shown in Table 3) was reported. To be able to discuss these results with respect to real conditions in the soil, the data from these parts of the research were supplemented by the analysis of biochar samples cultivated in selected representative soil samples (Table 3). The results indicate a decrease in the contents of W_{ORG} and the total contents of organic C and N for all biochar samples cultivated in the particular soils. The highest decrease was observed for cultivation in regosol (samples labelled with a suffix 2Y_R) and chernozem (samples labelled with a suffix 2Y_CH). Both these soil samples had lower original contents of total organic matter (regosol = 1.94 wt.%; chernozem = 2.45 wt.%), organic carbon (regosol = 1.09 wt.%; chernozem = 0.64 wt.%), and organic nitrogen (regosol = 0.19 wt.%; chernozem = 0.13 wt.%) compared to the remaining two soils, which were more fertile and agriculturally more attractive—fluvisol (W_{ORG} = 5.49 wt.%, organic C = 2.62 wt.%, organic N = 0.31 wt.%) and cambisol (W_{ORG} = 6.75 wt.%, organic C = 2.71 wt.%, organic N = 0.31 wt.%) [27]. According to these results, the application of biochar in less fertile soils with lower total organic matter content had a more significant impact on its final characteristics after the termination of the cultivation experiment. The data shown in Table 3 indicate the potential of the used biochar samples to act as soil conditioners, as they can release organic components and organic C and N (both are important elements of plant nutrition) into the surrounding soil. Comparison of the individual studied size fractions indicates the highest potential for the continual release of organic C and N in the case of coarser fractions of biochar. Moreover, these aspects are more pronounced in soil types with lower original content of SOM, which again correlates with the published literature [16,27–29]. The authors of these studies observed statistically significant soil conditioning effects of biochar, and these effects were more pronounced in the case of application to less fertile soils with lower W_{ORG} content. One year after the application of biochar to soil, Sovova et al. (2022) [27] observed a variation in the range 1.4–27.3 wt.% for the total organic matter content in biochar and 1.7–28.5 wt.% for the content of organic carbon. The most significant differences were observed for cultivation in less fertile, sandy, and textured soils. Yang et al. (2020) [28] observed that two years after biochar application in paddy soil, the organic carbon content of soil increased in the range of 4.0–26.7 wt.%. This author also identified the minor effects of biochar application on labile and microbial biomass-based carbon content in the studied soils. Comparable effects of biochar application on the content of SOM (1.2–12.8 wt.%) were also observed by the authors of the publication [29], who used an application dose of 10 wt.% of biochar (related to the total dry weight of soil). Chathurika et al. (2016) [8] investigated application doses of biochar in the range of 5–20 g per 1 kg of soil with/without synthetic soil fertilizers (ammonium phosphates). The most effective dose was 20 g of biochar per 1 kg of soil in combination with synthetic fertilization. Under these conditions, biochar application resulted in an increased soil cation-exchange capacity, P availability, and organic carbon content (in the range of units of %) in both studied soils (alkaline chernozem soil types). Taking into consideration our results from the soil cultivation experiments, the literature data, and the results obtained for the individual size fractions of biochar, we can conclude the following. Coarser fractions of biochar (fraction size of 2–4 mm and

higher) have a higher potential to act as soil stimulants, positively affecting the soil organic matter content and the content of organic C and N. Moreover, these coarser fractions are also more interesting from the practical point of view, as they can be easily applied on the field by the mechanical applicators with additional fertilization or during field tillage and have a lower possibility of being affected by natural conditions (wind, rain) during the application process.

Table 3. Elemental composition (C, N, H, O), total organic matter content (W_{ORG}), and total mineral content (W_{MIN}) of individual fractions of biochar samples [12], original non-fractionated biochar samples (NF), and biochar samples cultivated for 2 years in fluvisol (2Y_F), cambisol (2Y_C), regosol (2Y_R), and chernozem (2Y_CH).

Sample Label	W_{ORG} + (wt.%)	W_{MIN} + (wt.%)	Elemental Composition (wt.%)			
			C	N	H	O
BCH-S-A	67.86	32.14	59.97 ± 0.63	1.70 ± 0.11	0.81 ± 0.09	5.39 ± 0.28
BCH-S-B	72.93	27.07	67.66 ± 1.02	2.00 ± 0.08	0.94 ± 0.23	2.33 ± 0.44
BCH-S-C	78.96	21.04	71.72 ± 1.48	2.31 ± 0.08	2.00 ± 0.14	2.93 ± 0.56
BCH-S-D	77.42	22.58	65.66 ± 0.54	3.09 ± 0.09	1.61 ± 0.26	7.05 ± 0.29
BCH-S (NF)	77.01	22.99	66.22 ± 0.05	2.92 ± 0.11	2.71 ± 0.25	5.15 ± 0.06
BCH-S (2Y_F)	69.33	30.67	61.36 ± 0.66	1.53 ± 0.03	3.08 ± 0.22	3.35 ± 0.32
BCH-S (2Y_C)	69.81	30.19	62.48 ± 0.32	1.55 ± 0.06	2.61 ± 0.18	3.18 ± 0.26
BCH-S (2Y_R)	62.44	37.56	53.92 ±0.56	1.65 ± 0.11	2.72 ± 0.19	4.15 ± 0.31
BCH-S (2Y_CH)	63.86	36.14	55.18 ± 0.86	1.14 ± 0.06	3.06 ± 0.26	4.48 ± 0.18
BCH-N-A	71.44	28.56	63.40 ± 0.13	1.78 ± 0.18	1.57 ± 0.06	4.69 ± 0.12
BCH-N-B	82.56	17.44	74.48 ± 0.65	1.92 ± 0.12	1.63 ± 0.02	4.54 ± 0.26
BCH-N-C	91.08	8.92	84.34 ± 1.23	1.73 ± 0.10	2.62 ± 0.35	2.39 ± 0.56
BCH-N-D	81.23	18.77	73.27 ± 0.66	1.34 ± 0.08	2.64 ± 0.12	3.97 ± 0.29
BCH-N (NF)	82.62	17.38	70.48 ±0.25	2.89 ± 0.21	4.31 ± 0.36	4.94 ± 0.17
BCH-N (2Y_F)	70.87	29.13	63.49 ± 0.27	1.19 ± 0.11	3.83 ± 0.42	2.35 ± 0.13
BCH-N (2Y_C)	70.41	29.59	62.89 ± 0.42	1.20 ± 0.05	3.40 ± 0.18	2.92 ± 0.09
BCH-N (2Y_R)	66.23	33.77	50.14 ± 0.23	1.22 ± 0.18	3.10 ± 0.33	2.33 ± 0.12
BCH-N (2Y_CH)	59.03	40.97	52.82± 0.27	1.18 ± 0.14	2.93 ± 0.19	2.14 ± 0.22
BCH-CZ-A+B	70.35	29.65	47.89 ± 0.51	2.36 ± 0.14	4.54 ± 0.16	15.06 ± 0.28
BCH-CZ-C+D	78.98	21.02	56.40 ± 0.54	3.10 ± 0.18	3.38 ± 0.39	15.29 ± 0.37
BCH-CZ (NF) *	71.77	28.23	49.51 ± 0.46	2.52 ± 0.07	3.73 ± 0.21	16.01 ± 0.58

* Sample not applied in the realized cultivation experiment—results only for the original non-fractionated biochar; + recalculated on a dry sample without moisture.

The effect of biochar fraction size was further linked to the physicochemical properties of the individual biochar samples (Table 4). We observed that the higher capacity of the finest biochar particles to release inorganic ions has a direct effect on the selected physicochemical properties (mainly conductivity and SSA and also partially pH) of the surrounding soil [12,27]. The results of a previous study indicated a minor increase in pH and a more significant increase in conductivity with a decrease in biochar particle size. This trend was observed for all the studied biochar samples (BCH-N, BCH-S, and BCH-CZ), and the absolute values of both these physicochemical characteristics were dependent primarily on the source biomass used for biochar production, the pyrolysis conditions, and post-pyrolysis treatment [2,23,26,27]. The lower alkalinity of BCH-CZ is connected with the temperature of pyrolysis used for the production of this biochar (450–470 °C), which was lower compared to the other two samples (above 600 °C). The increase in pyrolysis temperature is, according to the literature [23,30,31], associated with the degradation of organic moieties in the original biomass, which results in the increased content of relatively temperature-stable alkaline inorganic salts (salts of alkaline metals and alkaline earth metals, e.g., K, Na, Mg, and Ca) in the produced biochar. Figure S2 (Supplementary Materials) indicates a dependence of the conductivities of the studied biochar samples on their mineral

ash content (W_{MIN}). There is a visual separation of individual studied biochar samples, which is significant proof of the importance of biochar mineral content on this parameter, and this has a direct connection to the production conditions and source biomass feedstock. More information regarding the production conditions of biochar and its corresponding content of mineral ions in the form of its ash content can be found in previously published literature [11]. This effect has already been described in the literature [32], where the authors observed that higher temperature induces loss of organic matter (structures based on organic C and N) but not of the minerals. For this reason, the amount of residual potassium cations increases relative to carbon. These inorganic salts based on alkaline macronutrients are soluble in an aqueous environment, which affects the conductivity and pH response of aqueous extracts (see Table 4). As was expected, the values of pH measured for the aqueous extract were higher for all the analyzed samples compared to the extracts obtained using 0.01 M $CaCl_2$ solution. This tendency can be explained by the effect of cation exchange, which in the case of 0.01 M $CaCl_2$ leads to partial release of H^+ ions, which correspondingly decrease the measured pH value. A more detailed discussion of the particle size and texture effect on the physicochemical characteristics of biochar can be found in our previously published research [12]. The observed interconnection of biochar texture with the pH and conductivity increase in aqueous extract is also in good agreement with published literature [11,33], where changes in both characteristics are explained by the increased content of soluble alkaline metals (e.g., K, Na, Mg, Ca) in the biochar structure.

Table 4. pH (H_2O and $CaCl_2$ methods), conductivity, and SSA (specific surface area determined by BET analysis [12]) of biochar fractions (data for individual fractions taken from our previous work [12]), original non-fractionated biochar samples (NF), and biochar samples cultivated for 2 years in fluvisol (2Y_F), cambisol (2Y_C), regosol (2Y_R), and chernozem (2Y_CH).

Sample Label	pH_{H_2O} (–)	pH_{CaCl_2} (–)	Conductivity (mS/cm)	SSA (m^2/g)
BCH-S-A	10.04 ± 0.14	9.29 ± 0.06	3.053 ± 0.006	171.6 ± 10.6
BCH-S-B	10.07 ± 0.02	9.26 ± 0.04	2.973 ± 0.040	209.2 ± 4.9
BCH-S-C	10.05 ± 0.10	9.15 ± 0.02	2.417 ± 0.049	288.4 ± 0.4
BCH-S-D	10.02 ± 0.02	9.14 ± 0.02	2.260 ± 0.010	313.1 ± 4.3
BCH-S (NF)	10.33 ± 0.01	10.07 ± 0.06	2.243 ± 0.101	201.7 ± 5.4
BCH-S (2Y_F)	7.99 ± 0.05	7.44 ± 0.03	0.234 ± 0.014	35.1 ± 6.7
BCH-S (2Y_C)	7.86 ± 0.03	7.24 ± 0.02	0.212 ± 0.008	33.1 ± 4.7
BCH-S (2Y_R)	7.62 ± 0.16	7.16 ± 0.04	0.263 ± 0.049	26.7 ± 7.5
BCH-S (2Y_CH)	7.67 ± 0.09	7.15 ±0.02	0.219 ± 0.024	31.2 ± 1.8
BCH-N-A	9.24 ± 0.21	8.41 ± 0.02	0.830 ± 0.006	54.3 ± 15.9
BCH-N-B	9.65 ± 0.08	8.44 ± 0.04	1.046 ± 0.008	165.0 ± 2.4
BCH-N-C	9.37 ± 0.02	8.34 ± 0.07	0.969 ± 0.013	168.2 ± 11.3
BCH-N-D	9.35 ± 0.01	8.24 ± 0 04	0.887 ± 0.003	139.7 ± 1.3
BCH-N (NF)	9.64 ± 0.02	9.12 ± 0.03	1.042 ± 0.219	168.2 ± 3.9
BCH-N (2Y_F)	8.13 ± 0.02	7.67 ± 0.05	0.184 ± 0.022	17.8 ± 2.6
BCH-N (2Y_C)	8.04 ± 0.03	7.54 ± 0.07	0.175 ± 0.012	17.6 ± 0.3
BCH-N (2Y_R)	7.65 ± 0.07	7.15 ± 0.04	0.144 ± 0.022	14.1 ± 1.9
BCH-N (2Y_CH)	7.54 ± 0.03	7.09 ± 0.03	0.174 ± 0.085	17.4 ± 1.5
BCH-CZ-A+B	8.56 ± 0.06	7.96 ± 0.04	3.447 ± 0.025	11.5 ± 0.8
BCH-CZ-C+D	7.16 ± 0.04	6.76 ± 0.03	3.227 ± 0.051	15.1 ± 4.4
BCH-CZ (NF) *	8.45 ± 0.11	**	3.299 ± 0.125	7.5 ± 0.3

* Sample not applied in the realized cultivation experiment—results only for the original not-fractionated biochar; ** value not determined.

To be able to discuss these results with respect to the real conditions in the soil, the obtained physicochemical characteristics of individual size fractions of biochar samples were compared with the data obtained from the analysis of biochar samples cultivated under driven conditions in selected representative soil samples (Table 4). The observed trends in measured pH and conductivities were straightforward. The original biochar

samples used in the cultivation experiments both had alkaline pH. Fidel et al. [34] identified the alkaline nature of biochar as the crucial aspect promoting its positive effects on soil properties and soil fertility due to the positive effect on specific interactions of the surface functional groups of biochar with soil organic matter. Moreover, the individual biochar samples obtained after the termination of the cultivation experiments exhibited significantly lower pH and conductivity compared to their initial values. This trend can be explained by the gradual leaching of soluble alkaline salts present in the inorganic content of both biochar samples (originally 22.99 wt.% for BCH-S (NF) and 17.38 wt.% for BCH-N (NF)) to the surrounding soil during the soil-irrigation cycles of individual corn plants cultivated during the experiment. According to the expectations, a more significant relative decrease in the values of pH and conductivity compared to the initial values was observed for the BCH-S sample—a sample with a higher initial content of inorganic salts. Comparison of the particular effects of individual soil samples used in the cultivation experiments indicated a more significant decrease in both pH and conductivity for biochar samples cultivated in regosol and chernozem (samples with suffix 2Y_R, respectively 2Y_CH), which were representatives of less fertile sandy soils with lower initial W_{ORG} content. According to the literature [35,36], the W_{ORG} content of the soil together with its cation exchange capacity are important parameters defining the actual soil buffering capacity. These aspects in total indicate that the observed trends for biochar samples cultivated in regosol and chernozem can be partially attributed to the low buffering capacity of these soil types, which leads to significant mineral and nutrient leaching to the subsoils or outside from the individual pots used during the cultivation experiment. On the other hand, fluvisol and cambisol (samples with suffixes 2Y_F and 2Y_C, respectively) had 3–5× higher initial W_{ORG} content, which led to their higher buffering capacity. This in consequence resulted in more effective soil conditioning by biochar, which also led to short-term soil fertilizing effects in the form of soluble inorganic salts based on macro- and microelements, which can be used by plants as nutrients.

Joseph et al. [37] defined three stages of biochar action in the soil. The initial stage (duration 1–3 weeks) is when the initial interaction with soil components takes place. Water entering the internal porous structure of biochar dissolves soluble organic (mainly low-molecular-weight residual non-pyrolyzed molecules) and inorganic mineral compounds (salts containing macro- and microelements). These released organic molecules can partially increase the content of dissolved organic matter and ions in soil solution, resulting in the increased conductivity and pH of soil [27]. As a consequence, a minor decrease in total W_{ORG} and a more significant decrease in pH and conductivity followed.

The visualization of the internal porous structure and morphology of studied biochar samples is shown in Figure S1 (Supplementary Materials). These data correlate well with determined values of SSA for the original biochar samples used in cultivation experiments. More discussion on this topic including the effect of biochar particle size on these characteristics can be found in our previous published work [12]. The observed results also showed a significant decrease in the measured SSA of biochar samples after cultivation, which indicates either the initial surface ageing of biochar or the transport of soluble soil fractions inside the internal pores of biochar. This effect was the most significant in soil samples having a lower W_{ORG} content (regosol, chernozem). Comparable tendencies can be found in the literature [38], where the authors described changes connected with biochar ageing in the soil. The most significant changes were found in the lateral surface of biochar exposed to the soil, which exhibited properties of a thin hydrophilic porous membrane on the surface of biochar.

The results indicate that the partially alkaline biochar with well-developed internal porous structures could represent promising enrichment solutions for acidic and partially acidic soil types, where biochar application leads to the partial increase and neutralization of soil pH. According to [37], the initial rapid release of organic and mineral compounds is followed by the following two stages, where a reactive surface on biochar is created by

enzymatic oxidation (stage 2), and long-term effects connected with gradual and extremely slow biochar decomposition take place (stage 3).

3.2. Total and Aqueous Extractable Macroelement and Microelement Contents

To be able to reveal the connection between the observed variation in the physicochemical characteristics of biochar samples and their contents of inorganic ions and to describe the effect of the size fraction of biochar on its physicochemical characteristics, multielemental analysis by ICP-OES was performed. Firstly, the contents of aqueous-extractable ions (macroelements—Na, K, Ca, Mg, P; microelements—Al, Fe, Zn, Mn, Cu, Cr, Ni) were determined. The obtained data represent the potentially accessible ions in the biochar structure, available to the soil after simple aqueous leaching, which could be used to reflect the situation in soil after irrigation or rain. These data were compared with their total contents, determined after the microwave digestion of the analyzed biochar samples. The aqueous-extractable contents of macroelements in the studied fractions of biochar varied in the range 0.1–1.4 mg/g of solid biochar sample, except for K (Figure 1A), whose content was significantly higher (1–5 mg/g of solid biochar sample). The major content of K in all obtained aqueous extracts from the biochar fractions emphasizes the role of K in alkaline pH response and the high conductivity of aqueous extract of individual biochar samples (Table 4). The pH and conductivity measurements performed on the aqueous extracts showed that the leachates from BCH-S and BCH-CZ were the most alkaline and also had the highest conductivities. The results shown in Figure 1A indicate similar trends in the content of aqueous-extractable K, as the amounts of K for the BCH-S and BCH-CZ were two to three times higher compared to BCH-N. The potential to release K can be also attributed to the SSA of the particular biochar sample, as for the more-textured materials having higher SSA (BCH-S), the contact surface area with the used solvent (water in the present work) is higher. On the other hand, the comparable amounts of ions released from fractions of BCH-CZ could rather be attributed to the source biomass used for the production of biochar (corn digestate, wheat straw, grass biomass) and the conditions used during its production (temperature below 500 °C) than its actual SSA. These findings correlate with the connection between extractable contents of K in biochar with both the corresponding alkaline pH response and the increased conductivity of biochar aqueous extracts [13,33]. K together with P and N are important plant nutrients. The increase in available K content in soil can positively affect plant growth processes (e.g., enzyme activation, stomatal activity, photosynthesis, and water and nutrient transport) and physicochemical soil properties (e.g., salinity, pH) [39]. The average aqueous soluble K content (0.014–0.048 μg/g) in surface soil is significantly lower compared to the detected values in studied biochar samples. The higher content of K in soil conditioners is thus very important even though the total K content in some soils could be high (15.6–17.3 mg/g); this is because K in such soils is mainly found in insoluble minerals resistant to chemical breakdown [40]. For this reason, plant available K is often not sufficient. A sufficient amount of plant-available K is considered to be more than 141 μg of K per g of soil [15]. In the case of BCH-S and BCH-CZ, the observed dependence of biochar fraction coarseness on the detected amount of aqueous-extractable K was indirect (Pearson correlation coefficient for BCH-S was $R = -0.845$ at a significance level of $\alpha = 0.05$ and for BCH-CZ was not determined); with increasing fraction size, the content of K decreased. In the case of the BCH-N sample, the dependence was similar, but the fraction BCH-N-D showed a break in the observed trend (Pearson correlation coefficient $R = -0.630$, at a significance level of $\alpha = 0.05$).

The data in Figure 1A also indicate the potential to release 5× higher contents of K, as the total contents of this ion obtained after the microwave digestion were higher by this order. This means that initially after biochar application as the soil conditioner, biochar has the potential to release nutrients to the surrounding soil in the form of salts containing K. This effect is, according to the literature [37], typical for the initial 1–3 weeks after application, as water entering biochar's internal porous structure dissolves soluble organic and inorganic mineral compounds. This initial rapid dissolution stage is more pronounced

in acidic and low-nutrient-containing soils [41], where, consequently, biochar has a higher initial soil conditioning impact.

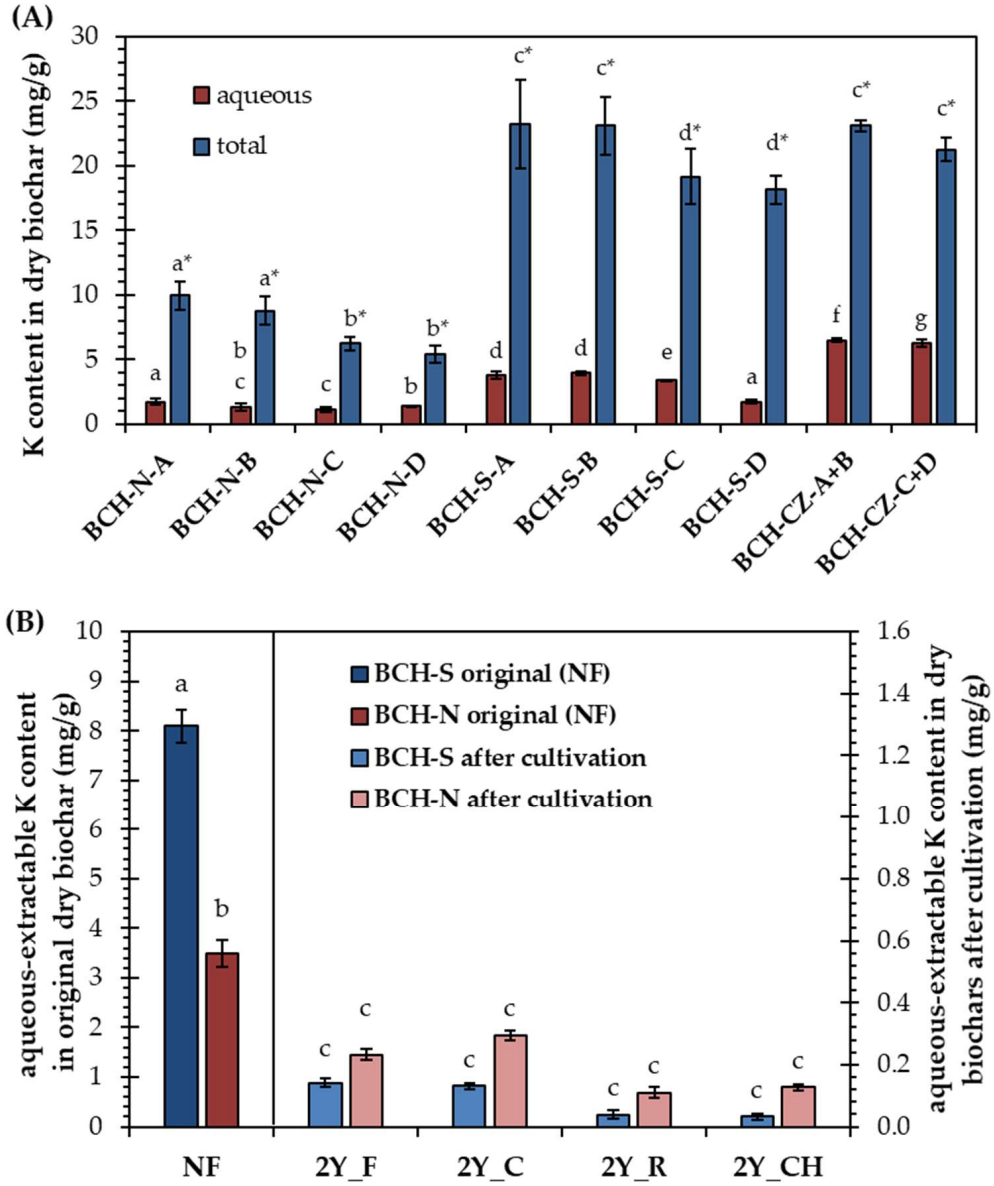

Figure 1. ICP-OES determination of (**A**) total and aqueous-extractable content of K in the individual fraction of biochar, (**B**) aqueous-extractable content of K in biochar samples before (original)/after cultivation in the individual used soils (F—fluvisol, C—cambisol, R—regosol, CH—chernozem); different letter indexes above columns indicate significant differences according to Tukey's test on significance level 0.05, indexes with * are connected to total K content in dry biochar.

Figure 1B shows the corresponding effect of the long-term cultivation (2 years) of selected biochar samples in the studied soils. The contents of aqueous-extractable K decreased after the termination of the cultivation experiment by more than 10× (on a relative scale, the released amount of original aqueous-extractable content was 98.2–99.6% for BCH-S and 91.5–96.8% for BCH-N). This result emphasizes the potential of biochar to act as a soil conditioner, providing the surrounding soil with an artificial short-term source of K. Taking into account the total determined contents of K (obtained after the microwave digestion, see Figure 1A), all the studied biochar samples had further potential to release K over time after additional ageing of their structure. The decrease in measured aqueous-extractable K content was more pronounced for the soil samples with lower W_{ORG}

content (regosol, chernozem), which, according to the literature [35,36], also have lower cation-exchange capacity. These types of soil have decreased soil buffering capacity, which results in minerals and nutrients leaching into the subsoils and/or outside of the pots used during the cultivation experiments. A more significant decrease in K content was observed for the BCH-S sample, which could be attributed to its higher original alkalinity, which supported the leaching of K. Concerning short-term soil conditioning effects relating to K, the highest original contents of this element were determined for finer fractions of BCH-S and BCH-CZ, which could represent more promising candidates for potential agronomical application into soil, where the inorganic nutrients increase is needed.

The research also focused on the aqueous-extractable contents of the remaining macronutrients (Na, Ca, Mg, and P). Figure 2A shows that Mg and Na were identified as the other significant aqueous-extractable macroelements detected in extracts from all the studied fractions of biochar. The aqueous extracts from BCH-CZ reflected a significant amount of Ca, while the leachates from the fractions of BCH-S and BCH-CZ contained detectable amounts of P. The highest overall content of aqueous-extractable macroelements was detected in BCH-CZ. In addition, aqueous extracts of the BCH-CZ also contained significantly higher contents of Ca, Na, and Mg compared to BCH-N and BCH-S. The explanation of these results is not simple, but from the comparison of BCH-N and BCH-S, as the materials produced at similar pyrolysis conditions, the significant role of SSA can be emphasized. This parameter is besides the pyrolysis conditions dependent on the composition of the original biomass feedstock used for biochar production. The BCH-S sample has almost twice higher SSA, which, together with its higher original inorganic content, resulted in a corresponding higher release of inorganic ions from its structure. Moreover, in the case of the BCH-CZ sample, the higher detected concentration of released macronutrients could be attributed either to its higher original inorganic content, to the different pyrolysis conditions (lower pyrolysis temperature) and composition of biomass (more heterogeneous, also containing digestate) used during its production, or also to its different pH response. The lower pH response of BCH-CZ resulted in a higher potential to dissolve and release its mineral contents compared to the remaining two biochar samples [41]. The other possible explanation could be related to the presence of significantly higher concentrations of acidic salts based on sulfates, carbonates, or carboxylates neutralizing the overall pH of BCH-CZ biochar. Moreover, the structure of BCH-CZ could also contain the acidic functional groups (e.g., carboxylic), which remain preserved due to the lower pyrolysis temperature used for the production of BCH-CZ (450–470 °C) compared to that used for BCH-N and BCH-S (above 600 °C). Additionally, ICP-OES analysis confirmed the presence of higher contents of low-molecular salts in fractions of BCH-S and BCH-CZ compared to fractions of BCH-N, which resulted in the higher detected conductivities of these two biochar samples.

The comparison of the aqueous-extractable content of macroelements with their total contents determined in solid samples (shown in Figure 2B) indicates similar trends for P, Mg, and Na. The total contents of these elements were approximately 10× higher compared to their aqueous-extractable amounts. This finding indicates, similarly as concluded for K, the potential to release these ions repeatedly into the surrounding soil during the initial stages after biochar application. Moreover, a comparison of the studied biochar samples from the perspective of their total macroelements contents showed five to ten times higher contents of Ca compared to its aqueous-extractable amounts and the highest contents of P in the extracts of BCH-S followed by BCH-CZ. Both these results support the potential of biochar to act as the macronutrient source at the initial stages after application to soil. The total contents of Ca and Mg were comparable between biochar samples, and the highest Na total content was detected for fractions of BCH-CZ. The differences between the studied biochar samples were less pronounced compared to the aqueous-extractable contents, which confirmed the crucial effect of biochar pH response on the aqueous-extractable contents of macroelements. The correlation between the obtained experimental data and published literature [41] indicates the potential of the studied biochar samples to directly influence soil properties after application as a soil supplement. The release of macronutrients and

mainly multivalent ions can contribute to soil aggregate formation, which is the key factor in terms of soil physical fertility. The high stability of the soil aggregate positively improves the water-holding capacity, water infiltration of soil, microbial colonization and microbial diversity, and germination and rooting of cultivated plants [26]. Moreover, the increased retention of macronutrients (Mg, K, Ca, Na) and the formation of complex structures with soil organic matter improves soil ion exchange capacity, which is a key factor in soil fertility and plant nutrient uptake [1,37,41]. From the agronomical point of view, BCH-S seems to be the most attractive candidate as a soil supplement, as it contains approximately 60 wt.% of C, 1 wt.% of N, 2 wt.% of K, and 0.1 wt.% of P, has a well-developed internal porous structure (Table 4—SSA between 171.6 and 313.1 m^2/g), and reflects the appropriate pH for agronomical utilization [34].

The results shown in Figure 2C indicate interesting trends in the aqueous-extractable contents of macroelements in the samples of BCH-S and BCH-N after cultivation in the studied soils. The data reflect an increase in the contents of aqueous-extractable Ca and oppositely a decrease in the content of Mg, Na, and P. Compared to the original values for non-fractionated biochar samples, the variations were more pronounced for the less fertile soil types (regosol—suffix 2Y_R and chernozem—suffix 2Y_CH). The observed tendencies of Mg, Na, P, and K (K shown in Figure 1B) can again be explained by the lower contents of W_{ORG} and organic C of these soils. Such soil has a lower cation-exchange capacity, which has a direct effect on its buffering capacity [35,36]. These types of soils reflect more significant release of minerals and nutrients into the subsoils, and/or in the case of our experimental design, also outside of the pots used during the cultivation experiments. The opposite trend for Ca indicates either the effect of pH or partial ageing of the biochar structure [38,41]. In our opinion, the effect of pH could be used as the probable explanation of the observed Ca trends, insofar as the solubility of the specific salt forms containing Ca increase with decreasing pH [42]. Moreover, the higher contents of aqueous-extractable Ca were determined for biochar samples cultivated in more acidic soil types (chernozem, regosol), which, according to the results in Table 4, also exhibited lower pH after the termination of cultivation. All this resulted in the higher solubility of Ca and its higher determined aqueous-extractable content in samples after the termination of cultivation.

Taking into consideration the effect of biochar fraction size, the results of ICP-OES indicated an indirect relation (calculated Pearson correlation coefficients shown in Table 5) between the increasing size of the biochar fraction and the contents of aqueous-extractable K, Na, and the sum of detected alkaline metals ($\Sigma_{(AM)}$ = K + Na + Ca + Mg). In contrast, a direct relation (calculated Pearson correlation coefficients shown in Table 5) with biochar fraction size was observed for aqueous-extractable Ca, Mg, and P. Statistically significant were the correlations for K, Ca, Mg, Na, $\Sigma_{(AM)}$, and P in the case of BCH-S biochar and for Mg and $\Sigma_{(AM)}$ for BCH-N biochar. The fractionation of the BCH-CZ sample resulted in two size fractions, and, for this reason, it was not possible to evaluate this sample statistically. The results shown in Table 5 for the size fractions of BCH-CZ represent a simple visual comparison of data. The data from the multi-elemental analysis are in good agreement with the research of Prasad et al. (2019) [11], who also described a positive correlation between the content of aqueous-extractable macronutrients (N, K, Mg, P, Na) and micronutrients (Cu, Zn, Mn) with the coarseness of various biochar samples. Person correlation analysis showed the relationship between the fractions size of individual biochar samples and the total contents of individual macroelements obtained after microwave digestion (Table 5). The correlation analysis showed an indirect relation between fraction size and almost all the analyzed macroelements as well as the determined sum of selected total contents of alkaline metals and alkaline Earth metals ($\Sigma_{(AM)}$). A statistically significant indirect correlation was detected in the case of BCH-N for almost all the macroelements and in the case of sample BCH-S for the correlation with K, $\Sigma_{(AM)}$, and P (for P observed direct correlation).

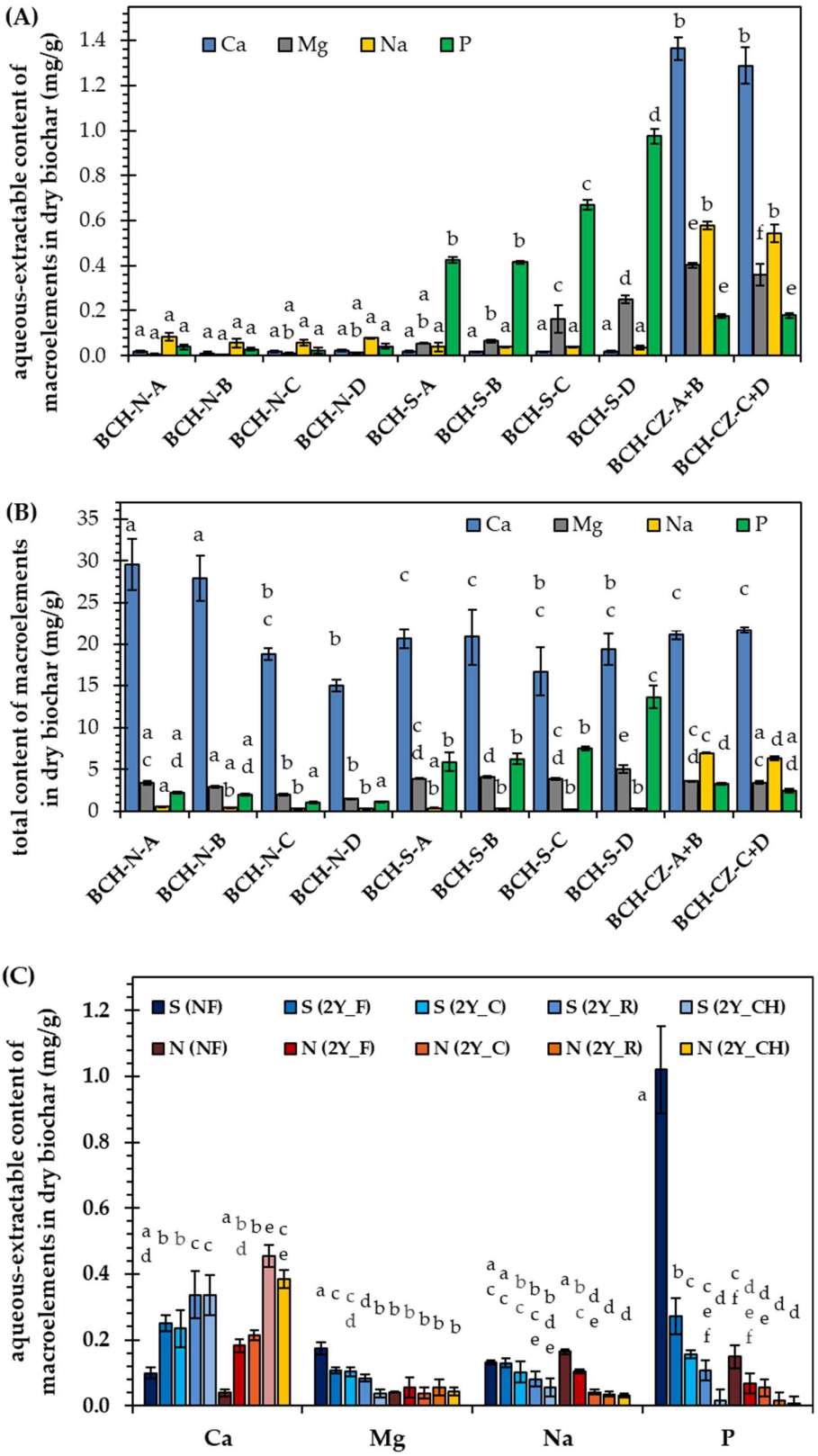

Figure 2. ICP-OES determination of (**A**) aqueous-extractable and (**B**) total contents of selected macroelements (K shown separately in Figure 1A) in the size fractions of biochar samples; (**C**) aqueous-extractable content of macroelements (K shown separately in Figure 1A) in the biochar samples before/after the cultivation in the individual used soils (F—fluvisol, C—cambisol, R—regosol, CH—chernozem); different letter indexes above columns indicate significant differences according to Tukey's test with significance level 0.05.

Table 5. Pearson correlation coefficients between the fraction size of studied biochar samples and the aqueous-extractable and total contents of macroelements ($\Sigma_{(AM)}$ is the sum of K, Ca, Mg, Na).

Biochar	K	Ca	Mg	Na	$\Sigma_{(AM)}$	P
			aqueous-extractable content (mg/g)			
BCH-N	−0.630	0.528	0.890	−0.172 $^{+}$	−0.781	0.117 $^{+}$
BCH-S	−0.845	0.784	0.960	−0.800	−0.847	0.932
BCH-CZ *	indirect	indirect	direct	indirect	indirect	direct
			total content (mg/g)			
BCH-N	−0.980	−0.968	−0.993	−0.961	−0.975	−0.887
BCH-S	−0.938	−0.701	0.751	−0.382	−0.904	0.877
BCH-CZ *	direct	indirect	indirect	indirect	indirect	indirect

* Pearson correlation analysis not determined, data commented from the visual comparison; $^{+}$ correlation coefficient is not significantly different from 0 ($\alpha = 0.05$).

The contents of aqueous-extractable micronutrients were almost three orders lower (in the range of μg/g—Figure 3) but still significantly higher compared to the sum of the contents of selected heavy metals (represented as the sum of the aqueous-extractable contents of As, Cd, Co, and Pb). This correlates well with the published natural content of micronutrients in soils [19]. Modern land cultivation practices create increased demands for the availability of soil micronutrients (e.g., Fe, Mn, B, Zn, Cu, Mo, Cl). Nevertheless, due to their limited bioavailability, the general concentration of micronutrients in soils is extremely low (units of ppm), yet their importance should not be neglected [43]. Another important observed aspect was the availability of micronutrients in soil, as these ions are not always present in solution, and their availability is restricted by the soil type, the content of organic matter, and the physicochemical conditions in the soil (pH, water content, redox potential) [19]. The results of aqueous leaching indicate the potential of biochar to serve not only as a soil conditioner positively affecting the physical properties of soil and microorganism activity but also as a minor source of micronutrients. Comparison between individual biochar samples showed similar contents of micronutrients detected in aqueous extracts of BCH-N and BCH-S and almost three times higher contents of Al, Fe, and Zn and two times higher contents of Mn and Cr in aqueous extracts of BCH-CZ. These results can be explained by the combined effect of the total mineral content of individual biochar samples and their pH response. Insofar as the fractions of the BCH-N sample showed significantly lower inorganic mineral content compared to the remaining two biochar samples (BCH-S and BCH-CZ), the significantly higher amounts of aqueous extractable micronutrients leached from BCH-CZ could be explained by the lower pH response of BCH-CZ [41].

Table S3 (Supplementary Materials) shows the potential of the studied fractions of biochar to leach Al, Fe, and Zn into the soil and provide important plant nutrients. In contrast, the aqueous-extractable contents of Al, Fe, and Zn were significantly lower (in the range of unit ug/g of dry biochar), which indicates the stronger bond of these microelements to the residual biochar matrix and/or their lower solubility [6,9,18]. The total and aqueous-extractable Zn contents detected for individual biochar fractions were significantly lower compared to the Al and Fe but comparable with the remaining microelements. The results obtained for aqueous-extractable ions and their comparison with their total contents in the biochar samples illustrate the additional short-term benefit of biochar application as the soil conditioner—specifically, the plant-nutrition potential, which is hidden below the high content of macro- and microelements bound on the residual biochar matrix. These initially bound ions can be released under certain conditions in soils, assuming the leaching effect of water (in the form of rain or irrigation) together with the action of plant roots, root exudates, and the effect of the microbial degradation of the biochar structure [37,44].

ICP-OES analysis showed that the aqueous-extractable contents of micronutrients in BCH-N and BCH-S obtained after the termination of the cultivation experiments decreased significantly, similarly to the situation for macronutrients. This can be explained by their

leaching into the surrounding soil, subsoil, and outside of the pots used for the cultivation experiments. In the original biochar samples, the micronutrient contents were far below 0.5 µg/g (related to the dry biochar weight), and, after the cultivation, they further decreased and, in most cases, reached the detection limits of the ICP-OES method.

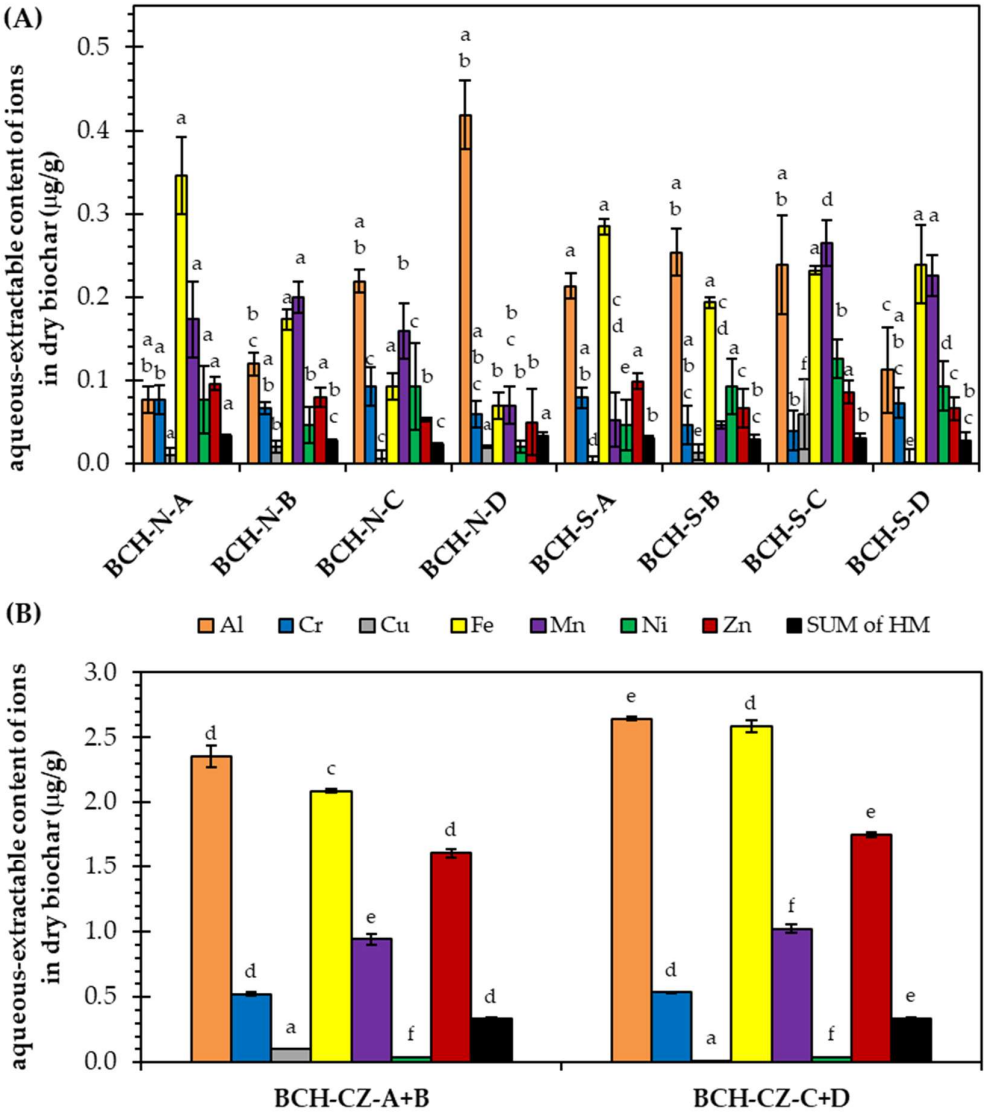

Figure 3. ICP-OES determination of the aqueous-extractable content of microelements in the fractions of analyzed biochar samples (**A**) BCH-N and BCH-S, (**B**) BCH-CZ; different letter indexes above columns indicate significant differences according to Tukey's test on a significance level of 0.05.

3.3. Extractable Contents of PAHs and Substituted Heterocyclic Compounds

Organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-dioxins, and furans (PCDD/Fs), are harmful substances, which can exert a toxic effect if taken up by organisms. Various PAHs can be co-generated with biochar as the side products of biomass pyrolysis [20,45]. These aromatic substances are, according to the literature [21], bound to the residual biochar matrix very strongly in various physical ways (non-covalent), and desorption is very limited. For these reasons, the total and bioavailable contents of PAHs in the biochar structure and their relation to the respective biochar size fraction seem to be crucial aspects driving the potential agronomical use of biochar as a soil conditioner.

Thirty-eight compounds were analyzed and quantified as part of the analysis of organic compounds present in biochar (PAH standard, 38 components, Absolute Stan-

dards, Inc.). These compounds were selected with certification in mind and also to monitor the presence of potential polycyclic compounds (substituted PAHs, nitrogen and sulfur heterocycles, and substituted naphthalenes) that are not required to be analyzed under EBC or International Biochar Initiative (IBI) certification [4]. Solvent extraction under elevated pressure was chosen as the extraction method. Toluene was used as the solvent, and a mixture of five deuterated PAHs standards [46] was added to each sample. The analytes of interest were grouped according to compound type (PAH, substituted naphthalenes, S-substituted and N-substituted heterocycles). Besides the total detected contents of all the above-mentioned groups of polycyclic organic structures, attention was also paid to comparison according to the fraction size of the biochar samples (Figure 4). The total determined PAHs concentrations in all the analyzed fractions of biochar samples were below 7 μg/g (7 ppm), thus below the IBI requirements (6–300 μg/g) and slightly over the EBC premium requirements values (4 μg/g) [4,15]. These contents of PAHs are below the values reported in the literature (9–300 μg/g) [47].

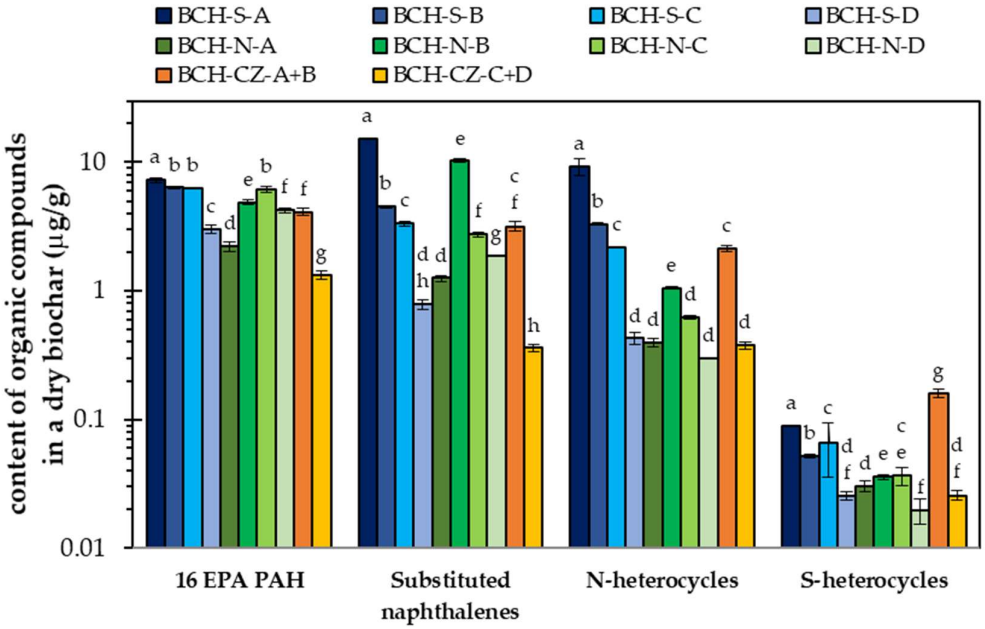

Figure 4. GC–MS characterization of the effect of biochar size fraction on the contents of PAHs and different groups of substituted aromatic and heterocyclic compounds; different letter indexes above columns indicate significant differences according to Tukey's test on a significance level of 0.05.

Hale et al. [22] reported that the bioavailable fraction of PAHs in biochar is approximately 1% of the total content, which is far below the above-mentioned limits. For this reason, we decided that it makes no sense to determine these types of organic molecules in the biochar samples obtained after the termination of the long-term cultivation experiments, as far as the original biochar samples already met the IBI and EBC defined limits. The data shown in Table 3 indicate the direct connection between biochar fraction size and the total contents of organic matter and organic carbon in the biochar structure. The observed decrease in the contents of 16 EPA PAHs (defined by the Environmental Protection Agency [48]), alkyl-substituted naphthalenes, and N-heterocyclic and S-heterocyclic aromatic compounds with an increase in biochar fraction size met our expectations based on literature research [20,21]. The only exception was the BCH-N sample, where the highest concentrations of individual organic components were found for the fractions BCH-N-B and BCH-N-C. Statistical evaluation using Pearson correlation analysis (Table 6) confirmed a statistically significant indirect relation between the fraction size of BCH-S and 16 EPA PAHS, substituted naphthalenes, and N-derivatized heterocycles as well as S-derivatized heterocycles. In the case of BCH-N, the correlation was not significant. The indirect correlation was achieved after the identification and exclusion of the BCH-N-A

as an outlier. After that, the remaining fractions of BCH-N even revealed a statistically significant correlation between fraction size and content of substituted naphthalenes and N- and S- substituted heterocycles.

Table 6. Pearson correlation coefficients (R) between fraction size of studied biochar samples and individual organic molecules, PAHs, and heterocycles.

Biochar	16 EPA PAHS	Substituted Naphthalenes	N-Heterocycles	S Heterocycles
BCH-S	−0.897	−0.901	−0.918	−0.960
BCH-N	0.557	−0.172 $^{+}$	−0.263 $^{+}$	−0.319
BCH-N ^{x}	−0.280 $^{+}$	−0.913	−0.918	−0.756
BCH-CZ *	indirect	indirect	indirect	indirect

^{x} Data with excluded fraction BCH-N-A; * Pearson correlation analysis not determined, data commented from the visual comparison; $^{+}$ correlation coefficient is not significantly different from 0 ($\alpha = 0.05$).

A similar relationship between biochar particle size and the content of PAHs and heterocyclic compounds was also observed by the authors of the publication [49]. In the presented results, the differences between the individual biochar size fractions were less pronounced, which can be attributed to the smaller size fractions used in the experiments. Moreover, a comparison between the individual biochar samples showed slightly higher contents of all the detected groups of aromatic organic compounds in the fractions of BCH-S followed by BCH-N. Only in the case of S-substituted heterocyclic compounds was the order BCH-S followed by the fractions of BCH-CZ. These observed dependences could be connected either to the effect of corresponding SSA of the particular biochar samples (highest values detected for fractions of BCH-S, followed by fractions of BCH-N) but also to the detected trends in W_{ORG} determined by thermogravimetry (Table 3). The highest content of organic matter was determined for the fractions of BCH-N biochar (71–91 wt.%), followed by BCH-S (68–79 wt.%) and BCH-CZ (70–79 wt.%). The observed differences between biochar samples are connected with variations in the pyrolysis conditions and also partially with differences in used biomass feedstock [4,20]. Both these producer-dependent parameters have direct effects on the development of aromatic structures in produced biochar samples, but the key factor is pyrolysis temperature [21]. PAHs and other derivatized heterocyclic compounds are formed either by carbonization followed by aromatization of original biomass feedstock (at temperatures below 500 °C) but also through a free radical pathway, which can be followed by pyrosynthesis into larger aromatic structures (at temperatures above 500 °C). As already described in previous sections of the manuscript, PAHs can be divided according to their molecular weight into LMW PAHs (2–3 benzene nuclei) and HMW PAH (4–7 benzene rings). The literature [22,44] describes HMW PAHs as a more serious issue, as they exhibit significantly higher toxicity compared to LMW PAHs. With increasing temperature and also pyrolysis residence time, LMW PAHs are transformed into HMW PAHs such as benzopyrene and benzoperylene [21], which are more toxic in nature. The formation of the individual PAHs is summarized in the reviews [20,21,43]. The data shown in Figure 5 indicate a direct connection between the relative content of HMW PAHs (compared to LMW PAHs) and the used pyrolysis temperature. The contents of HMW PAHs (containing four, five, and six cycles) are more pronounced for fractions of the BCH-N sample (produced at 720 °C) compared to those of the BCH-CZ (produced at 450–470 °C). These results are in good agreement with the data published by other authors [21,48].

Among the quantified compounds, naphthalene and alkyl-substituted naphthalene structures also significantly exceeded all other studied compounds in their detected concentration, which were orders of magnitude higher. However, these analytes are, in the vast majority, not included in the conditions of biochar certification. Other volatile compounds such as benzofuran, dibenzofuran, biphenyl, indane, indene, and others were also detected in fractions of the analyzed biochar samples. Again, these analytes are not listed in the certifications as substances, which need to be monitored in biochar. However, it is clear from the available literature that the smaller volatile molecules of the aromatic compound

type, as well as organic acids, alcohols, aldehydes, and many others, can influence various plant responses by mimicking plant hormones and thus promote or inhibit (depending on the concentration and the content of specific volatile organic compounds (VOC)) various plant responses—for example, seed germination, root growth, plant defense mechanisms against herbivores, nutrient uptake, and overall plant productivity. However, VOCs also affect soil microorganisms [21]. These effects are not long-lasting because VOCs are not capable of persistence in soil and quickly decompose, which is related to their release from the soil into the atmosphere [50].

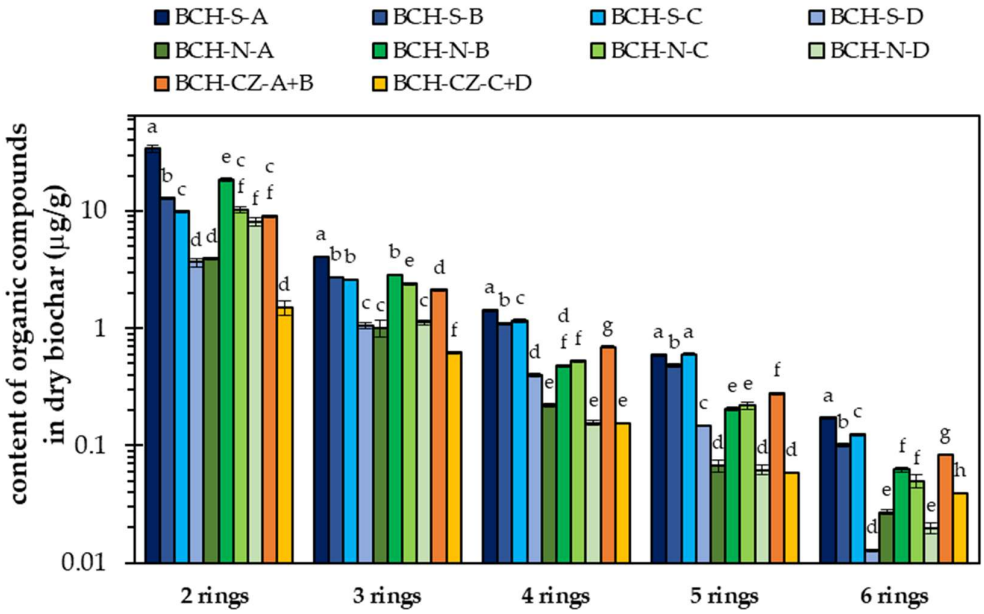

Figure 5. GC–MS characterization of the effect of biochar size fraction on the content of different types of polyaromatic compounds (based on the number of aromatic rings in the structure); different letter indexes above columns indicate significant differences according to Tukey's test on a significance level of 0.05.

3.4. Multivariate Statistical Characterization of Biochars

The results of particular analyses (discussed in Sections 3.1–3.3) were also further processed employing principal component analysis using Statistica software (software version 14.1.0.8, Tibco Software Inc.). A factor loadings plot and a projection of observations on the plane of principal components are presented in Figure 6. Biochar samples are projected onto the planes of principal components F1 and F2, which comprised in total 81.81% of the original variability of data. Multivariate analysis confirmed the results presented in previous chapters. A PCA plot revealed a clear separation of three biochar types corresponding to the three independent purchased samples. For this reason, the most crucial aspects driving biochar properties were the producers' dependent parameters, e.g., used biomass feedstock, pyrolysis conditions, used pre-treatments before the pyrolysis, etc.

PSA analysis also indicated that the BCH-N biochar was the sample with the highest content of organic matter, having the optimal values of SSA and pH, and 16 EPA PAH contents below the IBI and EBC limits. This material would be a perfect candidate for soil samples with lower organic matter content, which have a slightly acidic pH response, where this material can neutralize soil pH and act as the source of soluble organic matter. BCH-S biochar, on the other hand, had a lower content of organic matter, but it reflected the highest pH and SSA. This creates a BCH-S sample that is a solution in soil samples with a higher content of organic matter, which reflects the low mineral contents and low salinity. To sum up, the BCH-CZ sample had the lowest content of organic matter and the lowest SSA and pH. This material (produced at low pyrolysis temperatures) could be used

in neutral soils, where it can improve soil properties via the leaching of soluble fractions of organic matter.

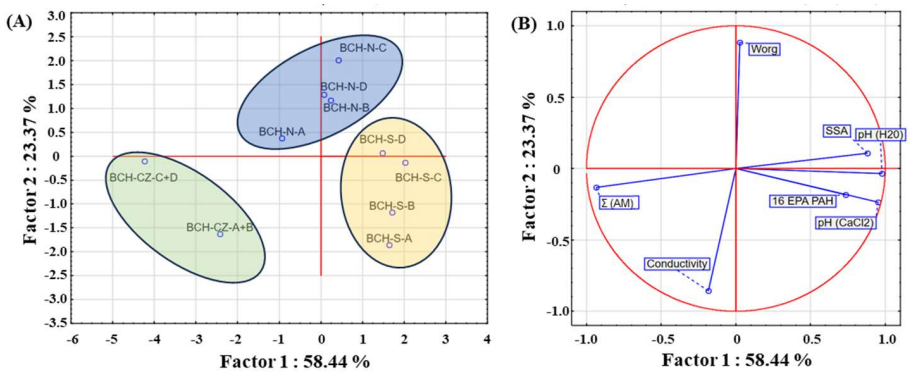

Figure 6. Projection of the observation scores (**A**) and variables (**B**) into factor plane of principal components F1 and F2.

At the same time, PCA analysis also revealed the effect of biochar fraction size on the chemical and physical properties of the studied samples. With increasing particle size, there was a gradual increase in the score of observation for component F2, which in our case corresponds to the total content of organic matter in the samples (W_{ORG}). On the other hand, a decrease in biochar fraction size resulted in a gradual increase in sample conductivity, which relates to increasing mineral content. Moreover, the data also revealed that the fractions with larger particle sizes exhibited slightly lower total aqueous extractable content of $\Sigma_{(AM)}$ (the sum of alkaline metals and alkaline Earth metals) and lower extraction efficiency for 16 EPA PAHs.

4. Conclusions

The agronomical use of biochar as a soil supplement has been increasing in popularity, even though significant research gaps still lack in-depth research. The results of this study show that the most crucial parameters affecting biochar properties are feedstock material and production conditions. Besides these producer-dependent parameters, the size fraction of biochar together with its specific surface area also influence the physicochemical properties of the material and its potential to release inorganic ions and aromatic and heterocyclic compounds. The results of the multi-elemental analysis indicated the crucial role of K as the main macroelement present in the inorganic mineral content of the studied biochar samples and also its major contribution to the alkaline pH response of aqueous biochar extracts. The analysis of biochar samples obtained after the termination of cultivation in soil confirmed that after the initial rapid leaching of K, the aqueous-extractable content of K in biochar decreased by more than 10×. Besides K, the remaining macroelements (Na, Ca, Mg, and P) and microelements (Al, Fe, Zn, Mn, Cu, Cr, Ni) were also detected in aqueous extracts of all the studied fractions of biochar samples. We identified a statistically significant indirect relation between an increase in the size fraction of biochar and the content of aqueous-extractable K and Na and the direct relation with the aqueous-extractable Ca, Mg, and P. Compared to the macronutrients, the detected contents of aqueous-extractable micronutrients were almost three orders lower (in the range of μg/g), and their dependence on the particle size of biochar was not consistent and statistically significant.

The research was also focused on the detection of polycyclic aromatic compounds and heterocycles, which can be co-generated during biochar production. The total determined PAHs concentrations in all the analyzed fractions of biochar samples were below 7 μg/g (7 ppm); thus, they were below the IBI requirements and almost equal to the values defined as premium requirements by EBC. Comparison with physicochemical characterization indicated a direct correlation of polycyclic aromatic contents with the total content of organic matter in biochar samples and a statistically significant indirect correlation with

particle size for BCH-S and BCH-CZ biochar samples and, after exclusion of the finest fraction BCH-N-A, also for BCH-N.

In conclusion, the finer fractions of biochar samples provided higher amounts of aqueous-extractable macro- and microelements, which can be further released into the soil. The middle-sized fractions (0.5–2 and 2–4 mm) of BCH-S were the most promising considering potential agronomical application, as they exhibited a well-developed internal porous structure, appropriate physico-chemical characteristics (pH, conductivity), PAHs contents far below the limits, approximately 60 wt.% of organic carbon, and high contents of available macro- and microelements. Moreover, the texture is more convenient for general agricultural practices, as it can be better applied during field tillage or by mechanical applicators with additional fertilization. When applied as a soil conditioner, the mineral contents of biochar can be gradually released. This provides macro- and microelements for the plants in the soil, a benefit that is in addition to the other well-known positive effects of biochar on soil properties. The results summarized in this work will provide necessary insights into the description of biochar´s mineral content, its connection to biochar texture, its physicochemical properties, and its potential to release nutrients into the soil. These findings could help in further assessment of biochar use as a soil conditioner in modern agriculture.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14102346/s1, Figure S1: SEM visualization of morphology and internal porous structure of used biochar samples (A) BCH-S (NF), (B) BCH-N (NF) and (C) BCH-CZ (NF) (data for used magnification 500×); Figure S2: Dependence of measured conductivity of individual fractions of biochar on mineral content (ash content, W_{MIN}); Table S1: The parameters of ICP–OES analysis and microwave digestion; Table S2: The parameters of GC–MS analysis; Table S3: Comparison of the aqueous-extractable and total contents of environmentally important micronutrients (Al, Fe, Zn) determined in analyzed fractions of biochar samples by ICP-OES.

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