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Biochar Particle Size and Texture–Parameters Affecting Its Agronomical Potential through the Effect on the Leaching of Organic Molecules and Macro- and Microelements

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Abstract: Biochar is a carbon-rich material that 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, the complex information on the direct dependence of biochar 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) are still not consistent. These aspects were addressed in our study. A multi-elemental analysis (ICP-OES) was used to access the information on the aqueous-extractable and total contents of inorganic macro- and macroelements in used commercial biochar samples (purchased from Sonnenerde GmbH, Novoterrra Sonnenerde GmbH, Biouhel.cz, s.r.o.). Potassium (K) was identified as the major macroelement, responsible for alkaline pH and the conductivity of biochar extract. Our results indicate an indirect relation between the size fraction of biochar and the content of extractable K, sodium (Na), and calcium (Ca) and a direct relation with the contents of phosphorus (P) and magnesium (Mg). As the total determined amounts of inorganic elements were significantly higher compared to aqueous-extractable amounts, we believe it could indicate the potential for repeated release to the surrounding soil. These findings were also confirmed by the analysis of biochar samples obtained after the cultivation (duration of 2 years) in selected representative soil samples from the Czech Republic (Cambisol, Fluvisol, Regosol, Chernozem). Moreover, 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 concentration of these types of organic compounds were far below the certified limits. We believe our in-depth analysis could provide the necessary insight into the description of biochar mineral content, its connection to biochar texture, corresponding physicochemical properties and potential availability to leach nutrients to the soil. These findings could help in further assessment of the potential applications of biochar in modern agriculture as a soil conditioner.

Keywords: agriculture; biochar; extraction; macro- and microelements; pH; conductivity; particle size; polyaromatic hydrocarbons; polycyclic organic compounds; soil conditioner; texture

1. Introduction

Biochar is a carbon-rich material produced by the thermal transformation of organic matter in an oxygen-limited atmosphere (pyrolysis). In recent years, the research interests related to the potential agronomical utilization of biochar as a soil conditioner have grown in importance. This was also probably stimulated by early studies of *Terra Preta* soil of the Amazon – a practical example of the unusually fertile black carbon-rich soil historically formed due to the agricultural practices of ancient farmers, which maintained its extraordinary fertility and physicochemical properties over the centuries [1,2].

The increasing population on the Earth bring about increasing demands on food production efficiency, plant yield and the maximal utilization of natural resources without undesirable wastes. All these aspects are resulting in the intensification of agricultural production and increasing requirements for soil fertility [3,4]. One of the possible solutions is the use of biochar as the soil conditioner because its application can positively influence the physical, chemical and biological properties of amended soil [5–7]. Biochar effect on soil properties is based mainly on its potential to reduce the release of greenhouse gasses [8], to affect the nutrient (P, N, Mg, Ca, K) leaching [9], to reduce heavy metal (e.g., As, Cu, Pb, Cr, Cd) mobility [10,11], to influence the content of soil organic matter content, to increase the ion-exchange capacity of soil [12], as well as to positively affect soil microorganisms [13]. Moreover, biochar can also influence the physical properties of soil through the effect on the soil structure, density, porosity, pH, conductivity and compactness. This effect is more pronounced mainly in coarse-textured soils, where biochar can significantly affect water infiltration rates [2].

The crucial characteristics of biochar such as its composition, development of internal porous structure, physicochemical properties etc. are closely related to the origin of used biomass feedstock materials (woody, non-woody), but also to the parameters of pyrolysis (temperature, residence time) and the pre-treatments used before the biomass transformation to the biochar [14–20]. All the aspects resulting in the high heterogeneity of produced material [21], brought about the tendency to create an industry standard, which could guarantee biochar sustainable properties and minimalize the potential risk of undesirable side effects and the presence of toxic substances in produced biochar. Therefore, in 2012 the European Biochar Certificate was established to create close cooperation between scientists and biochar producers [22]. Biochar particle size and texture are parameters, which can significantly influence mainly the physicochemical properties of biochar and the potential to release various inorganic and organic molecules. Nevertheless, the number of studies focusing on these important biochar parameters is limited. According to the authors [23–25], biochar particle size affects both soil physicochemical properties but also nutrient contents and their availability. These authors used biochar with variable size fractions (below 2, 3–6 and 6–9 mm) and they revealed a slight increase in soil organic matter content, a more significant increase in soil porosity and a decrease in the bulk soil density. The soil with the addition of biochar reflected an improvement in the soil mineral N, extractable P and K over the control sample. The most significant effect was observed for the smallest particle size (<3 mm) of biochar. The authors of the study [23] studied the extraction of individual nutrients from biochar and they revealed the highest contents of P, K and Mg for the smallest used biochar particle size fractions (0.15–0.60 mm). The study [24] confirmed the direct relationship between a decrease in biochar particle finest and the total extractable nutrients content. The author of the research [26] also identified the correlation with the pH. From the agronomical point of view, the soil available inorganic elements can be divided according to their importance into macroelements (N, P, K, Na, Ca, Mg) and microelements (Al, Fe, Zn, Mn, Cu, Cr, Ni). Additionally, macroelements can be further separated into primary (N, P, K) and secondary (Ca, Mg) [27]. In agriculture, macroelements are mostly applied in the form of salts, which often negatively affect the environment. These kinds of soil amendments can cause soil salinization or the leaching of soluble salts into watercourses [28]. The agronomically important micronutrients are present in natural soils in contents, which are three orders lower (in ppm), compared to the macronutrients. Despite this fact, their importance should not be neglected [29].

Another important group of chemicals, which need to be monitored in biochar are the polycyclic organic compounds such as polycyclic aromatic hydrocarbons (PAHs). These toxic substances can be co-generated during biochar production as the side products of biomass pyrolysis [29,30]. Probably the most important group of polycyclic aromatic compounds – PHAs can be further divided according to the molecular weight of individual substances into low molecular weight (LMW) PAHs, containing 2–3 benzene nuclei, and high molecular (HMW) PAHS, containing 4–7 benzene rings in the structure of a molecule. HMW PAHs exhibit many times higher toxicity than LHMW PAHs [31].

Despite the serious toxic effects of these compounds, their mobility is limited as they are strongly bound to residual biochar matrix. Hale et al. [32] defined that the bioavailable fraction of PAHs in biochar is approximately 1 % of their total content.

Due to the above-summarized findings, we focused the present study on an in-depth investigation of the effect of fraction size of used biochar, which together with the specific surface area are the important characteristics of biochar defining its texture. The texture of biochar, besides the producer-dependent parameters (e.g. used biomass feedstock, pyrolysis conditions), plays an important role in the final physicochemical properties of biochar (pH, conductivity, porosity) and its potential to leach various organic and inorganic compounds. The attention of our research was primarily focused on the total and aqueous extractable content of mineral structures based on macro- and microelements. Subsequently, the attention of the research was focused also on the discussion of the content and availability of several types of organic molecules (attention paid to the group of PAHs and derivatized heterocycles) in studied biochar samples as the harmful organic moieties can be co-generated during biochar production. We believe that the obtained set of basic biochar characteristics will provide the necessary insight into the interconnection of its texture (particle size, specific surface area) with the content and potential availability of various mineral nutrients and organic molecules to the surrounding soil, which could help in further assessment of the optimal application conditions of biochar 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, Austria) and NovoCarbo GmbH (NovoTerra, Germany) and both possess the European Biochar Certificate (EBC) [22]. The third sample was biochar produced by the company Biouhel.cz s.r.o. (Agrouhel, Czech Republic) for use in agriculture.

Biochar samples were initially air-dried at 45 °C for 48 hours to remove the absorbed moisture. The obtained dried samples were sieved by Vibratory Sieve Shaker AS 2000 (Retsch GmbH, 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 used biochar samples and their fractions are summarized in Table 1. Prior to the instrumental characterization, the obtained pretreated fractions of biochar were milled using a desktop swing mill HK 40 (H&K Laboratory equipment, Czech Republic) in HKMG6 zirconia oxide grinding vessel. The specific surface area (SSA) of these fractionated and dried biochar samples was characterized by employing Brunauer-Emmett-Teller (BET) analysis. The analysis is described in more detail in our previously published research [25].

Table 1. The summary of the 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			

The database of soil samples used in the work consisted of 4 different soil types from the Czech Republic (sampled from the upper humous horizon, depth of 30 cm). The first soil type was regosol (arid sandy soil) located in the area of Hodonin–Panov (48.878150°N, 17.132275°E), the second soil type was chernozem (arenic soil) located in the area of Zabcice (49.006433°N, 16.591367°E), the third soil type was cambisol (modal soil) located near Namest nad Oslavou (49.213263°N, 16.162481°E), and the last soil type was fluvisol (modal brown soil) located in the area of Ivan (49.921686°N, 16.561494°E).

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

2.2. Pot cultivation experiment

To be able to discuss the results of laboratory leaching experiments in broader consequences, the long-term pot cultivation experiments, where the individual samples of biochar were applied directly to the soil samples and cultivated under driven conditions with the presence of a model plant – *Zea mays* (corn) were also realized. For these purposes, the selected biochar samples were applied to the individual soil samples inside the semipermeable bags (4×4 cm, 5 g of biochar per bag) prepared from the polypropylene textile by impulse bag sealer. These bags were applied into pots (13x13x13 cm, maximal volume 1.5 litres), containing 1 kg of soil (dry weight of soil) mixed with perlite (4:1 in volume). Perlite was used to aerate the soil. Pots were placed into a grow box with controlled light exposure based on an average time of sunrise and sunset in the Czech Republic (6:15 – 18:30. Corn plants were cultivated in 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 continually monitored). After the termination of the pot cultivation experiment, the semipermeable bags with biochar were separated from the residual soil samples. Consequently, the biochar samples were air-dried at 45 °C in an oven and analyzed using the same set of instrumental techniques used for the characterization of original biochar samples.

2.3. Elemental analysis and thermogravimetry

The total content of organic matter (W_{ORG}) in studied fractions of dried and milled biochar samples was measured by thermogravimetric analyzer Q5000 (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 the ambient temperature to the temperature of 1000 °C (under air atmosphere). The used heating rate was 10 °C/min. The composition of basic organic elements (C, O, H, and N) was determined using a CHNS/O analyzer EA 3000 (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 realized 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

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 hour 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 also by using the standard calcium chloride method. 1 g of dried and milled fractions of biochar was dispersed in 10 mL 0.01 M $CaCl_2$ solution. After 1 hour of shaking, pH was measured directly in the suspension. All the analyzed samples were prepared in three independent replicates and the data presented in the manuscript are in the form of averaged values ± SD.

2.5. ICP–OES analysis

Multi-elemental analysis of aqueous-extractable content as well as the total content of inorganic elements in all studied biochar samples was carried out by the method 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). The calibration was performed by a method of standard addition into a blank sample. The setting of the ICP-OES analysis is shown in Table 2.

Table 2. The parameters of ICP–OES analysis and microwave digestion.

ICP–OES		**Microwave digestion program**		
Parameter	**Value**	**Step**	**Time (min)**	**Power (W)**
RP power	1350 W	1	2	250
Plasma gas flow rate	14 L/min	2	2	0
Auxiliary gas flow rate	0.5 L/min	3	6	250
Nebulizer gas flow rate	0.15 L/min	4	5	500
Nebulizer pressure	0.85 bar	5	5	Cooling
Detector voltage	550–900 V			

2.5.1. Content of aqueous-extractable inorganic elements

To determine the content of mobile (aqueous-extractable) elements, 0.5 g of individual biochar samples were dispersed in 10 mL of demineralized water. After 1 hour of shaking, the samples were filtered through 0.45 µm syringe filters (nylon membrane). The obtained filtrates were directly analyzed using ICP-OES. These analyses were performed on three individually prepared replicates and the results presented in the manuscript are in the form of averaged values ± SD.

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. 0.1 g of individual biochar samples 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 2. Digested samples were filtered through 0.45 µm syringe filters (nylon membrane) into the 25 mL volumetric flask and filled to the label with demineralized water. These samples were prepared in three independent replicates and analyzed using ICP–OES. The results are presented in the manuscript in the form of average value ± SD.

2.6. GC-MS analysis

The extraction was performed by a pressurized solvent extractor (OnePSE, Applied Sciences). The 1 g of sample was mixed with Hydromatrix (1:1) and transferred into the SPE extraction vessel. 10 µL of internal standard (10 ng/µL; deuterated PAHs standard, Absolute Standards Inc.) was added. Toluene (Sigma Aldrich, HPLC gradient grade) was used as an extraction solvent. The extraction was performed in 3 cycles (3 x 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. The GC–MS analysis was performed using Bruker EVOQ GC–TQ (Bruker, Germany). These samples were prepared in three independent replicates. The results are presented in the manuscript in the form of average value ± SD. Calibration was done by internal calibration method (deuterated standards mixture and PAHs mixture 38 components, Absolute Standards Inc). The utilized parameters of GC–MS analysis are summarized in Table 3.

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Table 3. The parameters of GC–MS analysis.

Parameter	Value
Duration of analysis	22 min
Helium flow rate	0.7 mL/min
Injection volume	1 μL, splitless
Injector temperature	270 °C
Column	DB-EUPAH (20 m x 0.180 mm x 0.14 μm)
Oven program	1) 1 min at 80°C 2) 15°C/min to 320 °C 3) 5 min, 320 °C
Ion source temperature	270 °C
MS mode	SIM, MRM
Detector	Triple quadrupole

2.7. Statistical analysis

Each experiment and instrumental analysis were performed at least in triplicate and the results presented in the manuscript are shown in the form of average values ± SD. The obtained experimental data were processed using a standard software package of Microsoft Excel (Microsoft Office Professional Plus 2019 software package) and Statistica (Tibco Software Inc.). The statistical significance of the presented results was determined using Dean-Dixon Q-test for the identification and rejection of outliers (significance level $\alpha \leq 0.05$). The obtained data were also further processed using the multivariate principal component analysis (PCA) based on the Pearson correlation method to determine the statistically significant parameters responsible for the observed trends in results.

3. Results

The main aim of the research was the investigation of the role of biochar particle size and texture on the crucial characteristics important for its possible agronomical utilization as a soil conditioner. The literature provides a detailed discussion on the importance of an appropriate selection of source biomass feedstock [2,17,33,34], biomass pre-pyrolysis treatment [35] and pyrolysis conditions [33,36,37] as the important prerequisites driving the final properties of produced biochar. The lack of information on the corresponding effects of particle size and biochar texture was already pointed out in our previously published research [25]. We identified minor effects of biochar texture on the main structural features of biochar but more significant effects on physicochemical properties, specific surface area and the total content of organic and inorganic constituents, possibly available to the soil after the application of biochar as a soil supplement. For these reasons, we have focused the present research on the in-depth investigation of the effect of biochar texture on the potential to release the inorganic components based on various macro- and microelements and as a minor task also discuss the potential availability of polyaromatic organic molecules (attention paid on the group of PAHs and heterocycles). These findings together with our previously published data could represent the crucial knowledge necessary for further assessment of its utilization and can help in the prediction of its agronomical potential as well as the definition of optimal form and dosage in agricultural use.

3.1. pH, conductivity, macroelements and microelements content

Previously published results [25] revealed the correlation of biochar particle texture with its physicochemical characteristics (pH, conductivity, organic and inorganic contents). We have reported the direct relation of biochar particle size fraction and the content of organic matter (and with the corresponding residual inorganic content), organic carbon and partially also organic nitrogen (data are shown in Table 4). The higher capability of the finest biochar particle to release inorganic ions has a direct effect on the physicochemical properties (pH, conductivity, ionic strength, water and ion-exchange capacity) of the surrounding soil [24,37,38]. In our previous study, we observed a minor increase in pH and a more significant increase in conductivity with a decrease in biochar particle fineness. This trend was observed for all the studied biochar samples (BCH-N, BCH-S and BCH-CZ).

Table 4. Elemental composition (C, N, H, O) and total organic matter content (W_{ORG}) of individual fractions of biochar samples [25].

Sample label	W_{ORG} (wt.%)	Elemental composition (wt.%)			
		C	N	H	O
BCH-S-A	67.86	59.97 ± 0.63	0.81 ± 0.09	5.39 ± 0.28	1.70 ± 0.11
BCH-S-B	72.93	67.66 ± 1.02	0.94 ± 0.23	2.33 ± 0.44	2.00 ± 0.08
BCH-S-C	78.96	71.72 ± 1.48	2.00 ± 0.14	2.93 ± 0.56	2.31 ± 0.08
BCH-S-D	77.42	65.66 ± 0.54	1.61 ± 0.26	7.05 ± 0.29	3.09 ± 0.09
BCH-N-A	71.44	63.40 ± 0.13	1.57 ± 0.06	4.69 ± 0.12	1.78 ± 0.18
BCH-N-B	82.56	74.48 ± 0.65	1.63 ± 0.02	4.54 ± 0.26	1.92 ± 0.12
BCH-N-C	91.08	84.34 ± 1.23	2.62 ± 0.35	2.39 ± 0.56	1.73 ± 0.10
BCH-N-D	81.23	73.27 ± 0.66	2.64 ± 0.12	3.97 ± 0.29	1.34 ± 0.08
BCH-CZ-A+B	70.35	47.89 ± 0.51	4.54 ± 0.16	15.06 ± 0.28	2.36 ± 0.14
BCH-CZ-C+D	78.98	56.40 ± 0.54	3.38 ± 0.39	15.29 ± 0.37	3.10 ± 0.18

Fidel et al [39] identified the alkaline nature of biochar as the crucial aspect promoting the positive effects on soil properties and soil fertility due to the positive effect on specific interactions of the surface functional groups of biochar with the soil organic matter. Joseph et al [2] defined three stages of biochar action in soil, the initial stage (duration 1–3 weeks), where 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-pyrolysed 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 [37]. For this reason, the application into the acidic soil types could represent the possible solution for the partial increase of soil pH to the neutral region. According to [2] the initial rapid release of organic and mineral compounds is followed by the following two stages, where the 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).

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 [33,40,41] 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 produced biochar. These salts are soluble in an aqueous environment, which affects the conductivity and pH response of aqueous extract (see Table 5). A more detailed discussion of the particle texture effect on the physicochemical characteristics of biochar can be found in our previously published research [25]. The observed interconnection of biochar texture with the pH and conductivity increase of aqueous extract is also in good agreement with published literature [23,24], where the changes in both characteristics are explained by the increased content of soluble alkaline metals (e.g., K, Na, Mg, Ca) in biochar structure. To be able to reveal the connection of the observed variation in physicochemical conditions of biochar samples with their content of inorganic ions and to describe the effect of the size fraction of biochar on its physicochemical characteristics, multi-elemental analysis by ICP-OES was utilized.

Table 5. pH (H_2O and $CaCl_2$ methods), conductivity and SSA of biochar fractions [25].

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-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-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

The ICP-OES analysis was used in two individual methodological approaches. Firstly, the content of aqueous-extractable ions (macro elements – Na, K, Ca, Mg, P; microelements – Al, Fe, Zn, Mn, Cu, Cr, Ni) was determined. The obtained data represent the potentially accessible ions in biochar structure, available to the soil environment after irrigation or rain. These data were compared with their total contents, determined after the microwave digestion of the analyzed biochar samples. The results of aqueous-extractable contents of macroelements in the studied fractions of biochar samples varied in the range between 0.1–1.4 mg/g of solid biochar sample (Figure 2a), except for K (Figure 1), which content was significantly higher (1–5 mg/g of solid biochar sample). The detected major content of K in all obtained aqueous extracts from the biochar fractions emphasises the role of K in alkaline pH response and high conductivity of aqueous extract of individual biochar samples (Table 5). The pH and conductivity measurements performed on the aqueous extracts from the biochar fractions indicated the most alkaline nature of the leachates from BCH-S and BCH-CZ, which also reflected the highest conductivities. The results shown in Figure 1 indicate similar trends in the determined content of aqueous-extractable K, as the determined amount of K for BCH-S and BCH-CZ biochar samples was 2–3x higher compared to BCH-N. These findings correlate with the literature-described [23,26,27] connection of K extractable content in biochar with the corresponding alkaline pH response and increased conductivity of biochar aqueous extracts. K together with P and N represents important plant nutrition. The increase of available K content in soil can positively affect plant growth processes (e.g. enzyme activation, stomatal activity, photosynthesis or water and nutrient transport) and physicochemical soil properties (e.g. salinity, pH) [42]. 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 the soil conditioners is thus very important even though the total K content in some soils could be high (15,6–17.3 mg/g), it is mainly found in insoluble minerals resistant to chemical breakdown [43]. For this reason, the 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 [30]. The observed dependence of biochar fraction coarseness on the detected amount of aqueous-extractable K was in the case of BCH-S and BCH-CZ indirect (Pearson correlation coefficient for BCH-S was R = -0.845, for BCH-CZ was not determined), with increasing fraction size, the content of K was decreasing. 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).

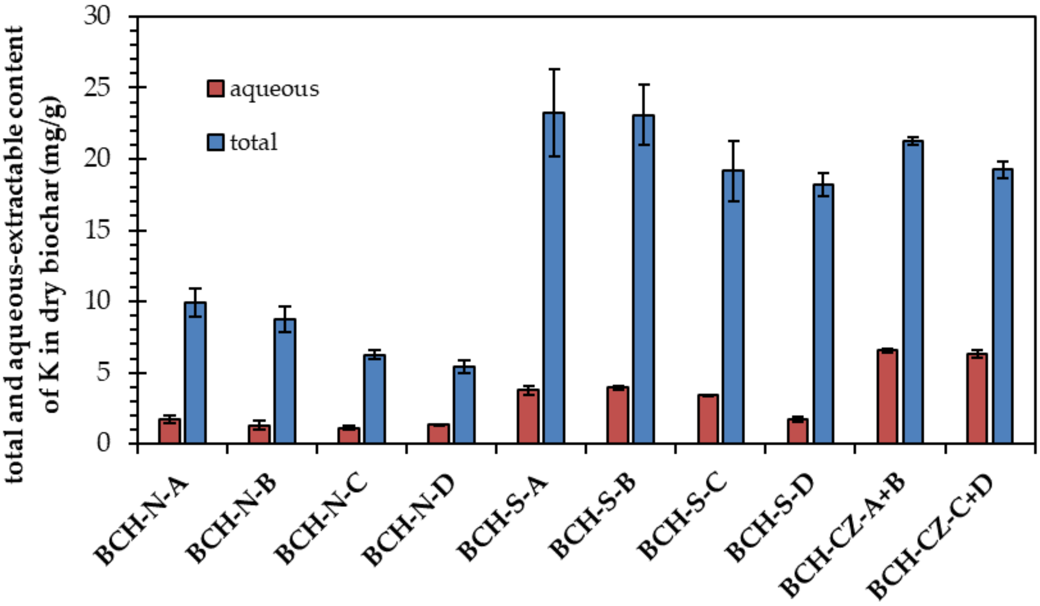

Figure 1. ICP-OES determination of the total and aqueous-extractable content of K in biochar.

The data in Figure 1 also indicate the potential to release 5x higher contents of K, as the total contents of this ion obtained after the microwave digestion was by this order higher. This means, that initially after biochar application as the soil conditioner, biochar has the potential to release nutrition to the surrounding soil in the form of salts containing K. This nutrition effect of biochar is according to the literature [2] typical for the initial 1–3 weeks after the application to the soils, as water entering biochar internal porous structure dissolves soluble organic and inorganic mineral compounds. This initial rapid dissolution stage is more pronounced and faster in acidic and low-nutrient soils [44], where consequently biochar has a higher initial nutrition impact.

The attention of research was further focused on the aqueous-extractable content of remaining macronutrients (Na, Ca, Mg and P). The results shown in Figure 2a indicate Mg and Na as the additional significant aqueous-extractable macroelements detected in the extracts originating from all the studied fractions of biochar samples. The aqueous extracts from BCH-CZ reflected a significant amount of Ca and leachates from the fractions of BCH-S and BCH-CZ contained a detectable amount of P. The highest overall content of the aqueous-extractable macroelements was detected in BCH-CZ. For the fractions of BCH-CZ, the content of K in extracts was 2x higher compared to BCH-S and 3x higher compared to the BCH-N sample. In addition, aqueous extracts of the BCH-CZ sample contained also significantly higher contents of Ca and Na, Mg compared to BCH-N and BCH-S. The explanation of these results is not simple but could be connected with the pH response of individual studied biochar samples. The lower pH response of BCH-CZ resulted in a higher potential to dissolve and leach the mineral content present in the fractions of BCH-CZ compared to the remaining two biochar samples [45]. 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) in contrast to the biochar samples BCH-N and BCH-S (above 600 °C). Additionally, the ICP-OES analysis confirmed the higher contents of low-molecular salts present in fractions of BCH-S and BCH-CZ compared to the fractions of BCH-N, which resulted in higher detected conductivities of these two biochar samples.

The comparison of data obtained for 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 detected total contents of these elements were approximately 10x higher compared to their aqueous-extractable amounts. This finding indicates, similarly as concluded for K, the potential to release these ions to surrounding soil repeatedly at the initial stages after biochar application as the soil conditioner. Moreover, the comparison of studied biochar samples from the view of their total macroelements content showed 5–10x higher content of Ca compared to its aqueous-extractable amounts and the highest content 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 the application to soil. The total content 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 our assumption of the crucial role of biochar pH response on the aqueous-extractable contents of microelement. The correlation of obtained experimental data with published literature [44] indicates the potential of studied biochar samples to directly influence the soil properties after the application as soil supplements. The macronutrient release and mainly the multivalent ions can contribute to the soil aggregates formation, which is the key factor in terms of soil physical fertility. The high stability of soil aggregate positively improves the water-holding capacity, water infiltration of soil, microbial colonization and microbial diversity, germination and rooting of cultivated plants [36]. 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 nutrition uptake [1,2,44]. From the agronomical point of view, the BCH-S sample seems to be the most attractive, 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 5 – SSA between 171.6 and 313.1 m^2/g) and reflects the appropriate pH for the agronomical utilization [39].

Taking into consideration the effect of the biochar size of fraction, the results of ICP-OES indicated an indirect relation (calculated Pearson correlation coefficients shown in Table 6) of the increasing size of biochar fraction to the content of aqueous-extractable K, Na and sum of detected alkaline metals (Σ_{AM} = K+Na+Ca+Mg). Oppositely the direct relation (calculated Pearson correlation coefficients shown in Table 6) with biochar fraction size was observed for the aqueous-extractable Ca, Mg and P. Statistically significant were the correlations for K, Ca, Mg, Na, Σ_{AM} and P in the case of BCH-S biochar and for Mg and Σ_{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 6 for the fractions of BCH-CZ represent a simple visual comparison of data obtained for the particular fractions. The data from the multi-elemental analysis are in good agreement with the research of Prasad et al. [24], who also described the positive correlation between the content of aqueous-extractable macronutrients (N, K, Mg, P, Na) and micronutrients (Cu, Zn, Mn) to the coarseness of various biochar samples.

Table 6. Pearson correlation coefficients (R) between the fraction size of studied biochar samples and the aqueous-extractable and total contents of macroelements (Σ_{AM} is the sum of K, Ca, Mg, Na).

Biochar	**K**	**Ca**	**Mg**	**Na**	**Σ_{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.

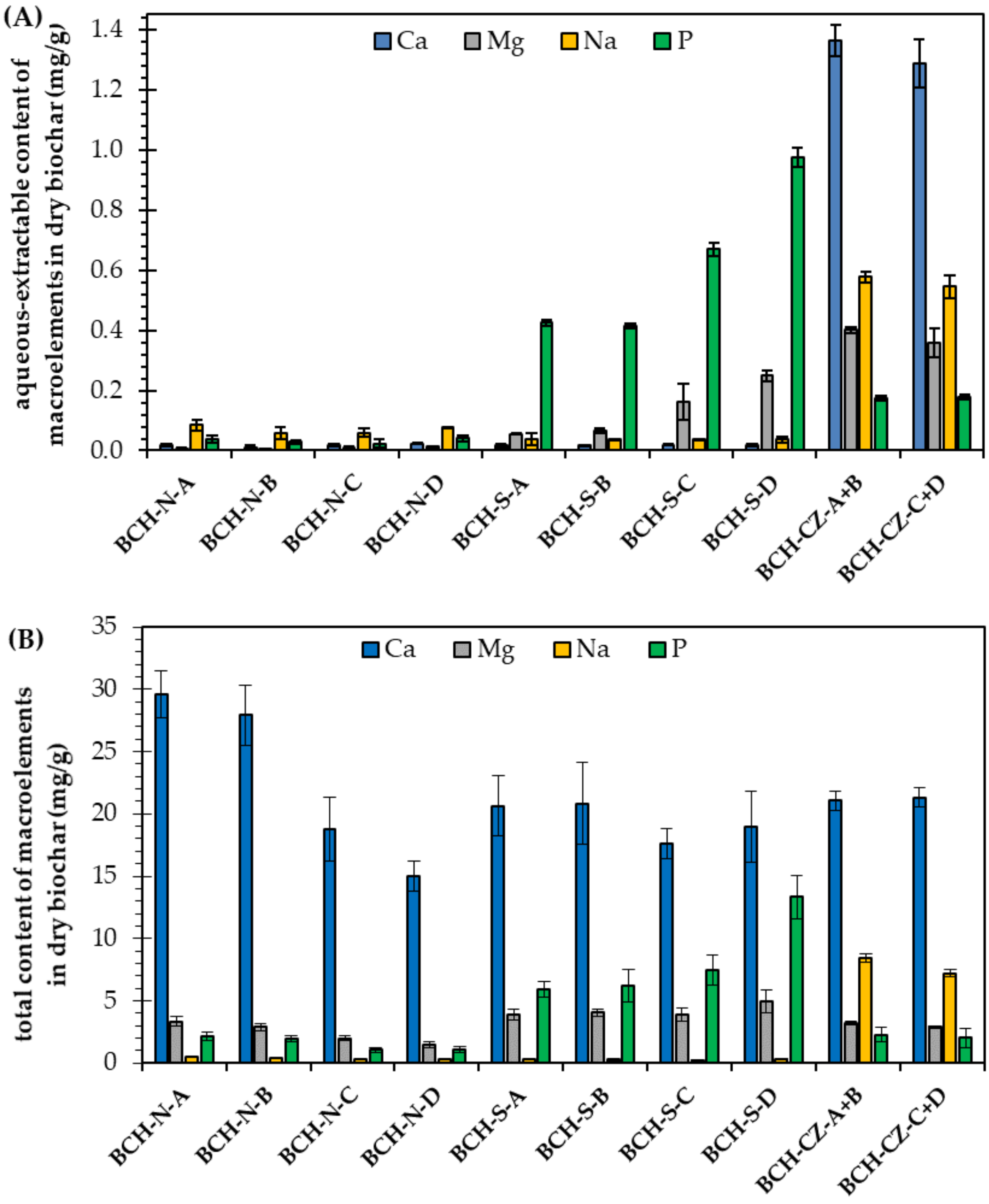

Figure 2. ICP-OES determination of the (A) aqueous-extractable and (B) the total content of selected macroelements (K shown separately in Figure 1).

The statistical Person correlation analysis was performed also to show the relationship between the fractions size of individual biochar samples and the total contents of individual macroelements obtained after the microwave digestion (Table 6). The correlation analysis showed an indirect relation of fraction size to almost all the analysed macroelements as well as the determined sum of selected total contents of alkaline metals and alkaline Earth metals (Σ_{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, Σ_{AM} and P (for P observed direct correlation).

The detected 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 content of selected heavy metals (represents the sum of aqueous-extractable content of As, Cd, Co and Pb). This correlates well with the published natural content of micronutrients in soils [29]. The modern way of land cultivation practices creates increased demands for the availability of soil micronutrients (e.g., Fe, Mn, B, Zn, Cu, Cr, Mo, Cl, Ni). Nevertheless, the common concentration of micronutrients in soils is extremely low (units of ppm) and their importance should not be neglected [46]. 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 physicochemical conditions in soil (pH, water content, redox potential) [29]. The result of aqueous leaching applied on individual studied biochar samples indicates their potential to serve not only as the soil conditioner affecting positively the physical properties of soil and microorganism activity but also as a minor source of micronutrients. The comparison between individual biochar samples showed similar contents of micronutrients detected in aqueous extracts of BCH-N and BCH-S samples and almost 3x higher content of Al, Fe and Zn and 2x higher content of Mn and Cr for the 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. As far 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 observed significantly higher amounts of detected aqueous extractable micronutrients leached from BCH-CZ could be again explained by the lower pH response of BCH-CZ [45].

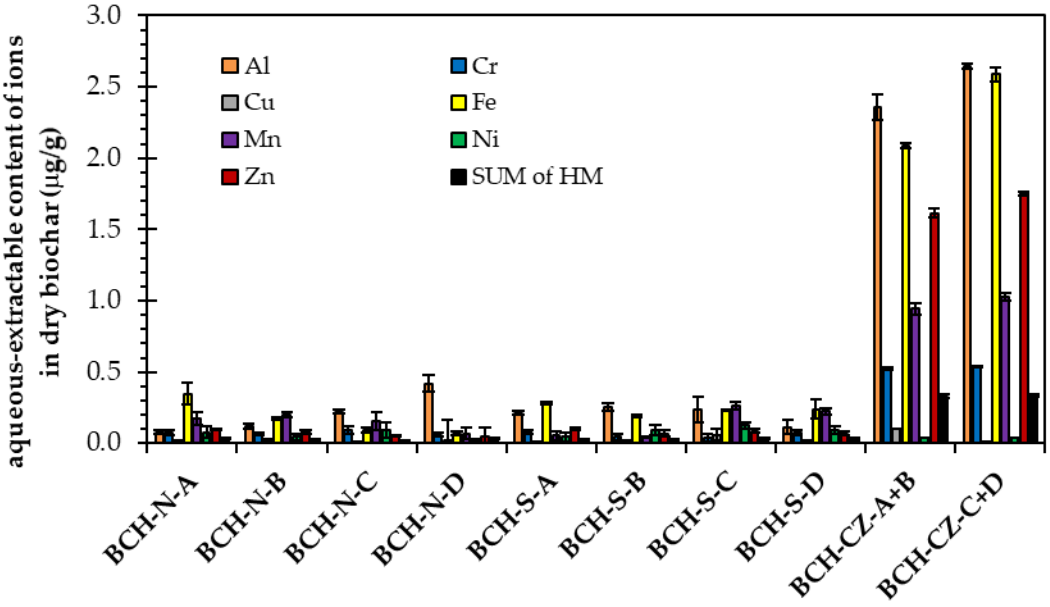

Figure 3. ICP-OES determination of the aqueous-extractable content of microelements in the fractions of analyzed biochar samples.

To access more deeply the potential of studied fractions of biochar samples to leach Al, Fe and Zn to the soil and provide important plant nutrition, Table 7 provides the comparison of their aqueous-extractable and total contents in the studied fractions of biochar samples. These data indicate comparable total contents of Al and Fe as were detected for macroelements in studied biochar samples. On the other hand, 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 higher bond strength of these microelements to the residual biochar matrix [9,13,29]. 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 the aqueous-extractable ions and their comparison with their total content in the biochar samples have illustrated the additional short-term benefit of biochar application as the soil conditioner – 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 possibly released at certain conditions in soils assuming the leaching effect of water (in the form of rain or irrigation) together with the action of plant roots and root exudates, and the effect of microbial degradation of biochar structure [2,47].

Table 7. Comparison of the aqueous-extractable and total content of environmentally important micronutrients (Al, Fe, Zn) determined in analyzed fractions of biochar samples by ICP-OES.

Sample label	Al		Fe		Zn	
	aqueous (µg/g)	total (mg/g)	aqueous (µg/g)	total (mg/g)	aqueous (µg/g)	total (mg/g)
BCH-N-A	0.077 ± 0.015	5.56 ± 0.41	0.346 ± 0.008	6.12 ± 1.11	0.096 ± 0.008	0.27 ± 0.08
BCH-N-B	0.120 ± 0.014	3.07 ± 0.34	0.173 ± 0.012	2.36 ± 0.21	0.080 ± 0.012	0.24 ± 0.03
BCH-N-C	0.219 ± 0.014	1.25 ± 0.17	0.093 ± 0.002	1.38 ± 0.14	0.053 ± 0.022	0.13 ± 0.02
BCH-N-D	0.419 ± 0.006	1.05 ± 0.08	0.070 ± 0.002	0.74 ± 0.09	0.050 ± 0.029	0.11 ± 0.02
BCH-S-A	0.213 ± 0.017	1.41 ± 0.11	0.284 ± 0.010	1.70 ± 0.27	0.099 ± 0.009	0.09 ± 0.02
BCH-S-B	0.253 ± 0.003	0.77 ± 0.09	0.193 ± 0.006	0.83 ± 0.07	0.067 ± 0.023	0.16 ± 0.04
BCH-S-C	0.239 ± 0.009	0.40 ± 0.04	0.232 ± 0.011	0.49 ± 0.06	0.086 ± 0.029	0.10 ± 0.01
BCH-S-D	0.113 ± 0.010	1.20 ± 0.13	0.239 ± 0.067	0.57 ± 0.11	0.066 ± 0.011	0.12 ± 0.02
BCH-CZ-A+B	2.356 ± 0.011	10.04 ± 0.23	2.091 ± 0.018	13.21 ± 0.62	1.613 ± 0.032	1.89 ± 0.08
BCH-CZ-C+D	2.645 ± 0.015	11.51 ± 0.58	2.587 ± 0.050	13.68 ± 0.26	1.753 ± 0.143	1.92 ± 0.13

3.2. GC-MS analysis

The 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 [30,48]. These aromatic substances are according to the literature [31,32] bound to the residual biochar matrix very strongly in various physical manners (non-covalent) and the desorption process is very limited. For these reasons, the knowledge of the total and bioavailable content of PAHs in biochar structure and finding the interconnection with actual biochar size fraction, seem to be crucial aspects driving the potential of possible biochar agronomical utilization as the 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 Standards, Inc.). These compounds were selected with certification in mind and also to monitor the presence of other 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 [22]. Solvent extraction under elevated pressure was chosen as the extraction method [49]. Toluene was used as the solvent and a mixture of five deuterated PAHs standards [50] was added to each sample. The analytes of interest were grouped according to compound type (PAH, substituted naphthalenes, S-substituted and N-substituted heterocyclic compounds). Besides the total detected contents of all the above-mentioned groups of polycyclic organic structures, attention was paid also to the mutual comparison according to the fraction size of the biochar samples (Figure 4).

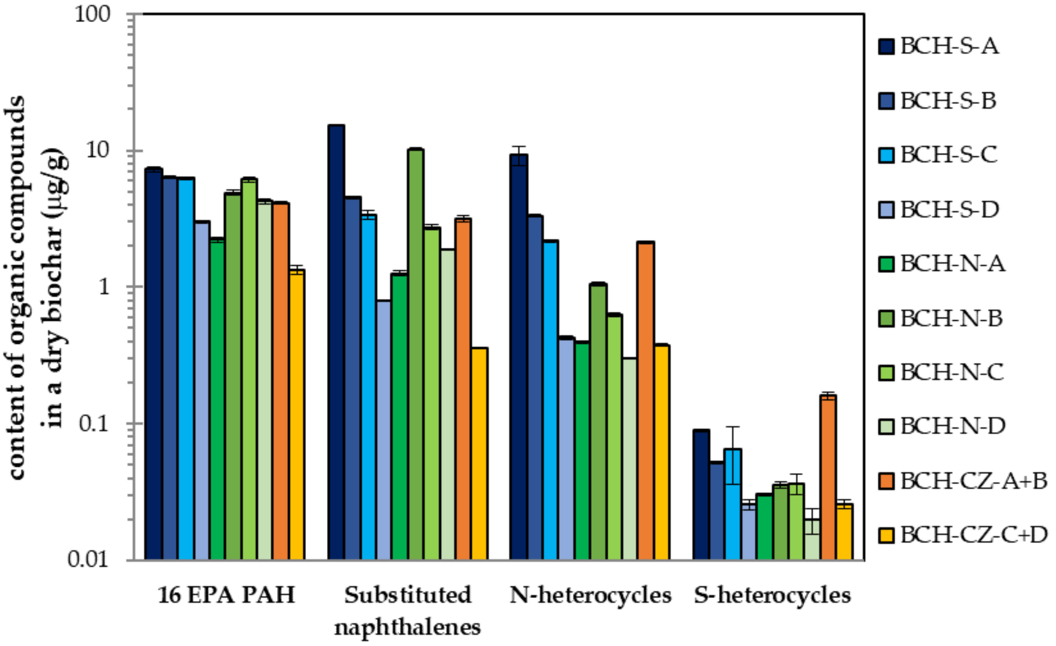

Figure 4. GC–MS characterization of the effect of biochar size fraction on the content of PAHs and different groups of substituted aromatic and heterocyclic compounds.

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) [22,30]. These contents of PHAs are below the values reported in the literature (9–300 µg/g) [51]. Hale et al. [32] defined that the bioavailable fraction of PAHs in biochar is approximately 1% of the total content, which is far below the above-mentioned limits. The data shown in Table 4 indicated the direct connection of biochar fraction size to the total content of organic matter and organic carbon in biochar structure. The observed general decrease in the contents of 16 EPA PAHs (defined by the Environmental Protection Agency [52]), alkyl-substituted naphthalenes, N-heterocyclic and S-heterocyclic aromatic compounds with the increase in fraction size of biochar met our expectations based on literature research [30,31,53]. The only exception was found BCH-N sample, where the highest concentrations of individual organic components were found for fractions BCH-N-B and BCH-N-C. The statistical evaluation using the Pearson correlation analysis confirmed the statistically significant indirect relation between the fraction size of BCH-S and 16 EPA PAHS, substituted naphthalenes, N-derivatized heterocycles as well as S-derivatized heterocycle. In the case of BCH-N, the correlation was not significant. The indirect correlation was achieved after the identification and exclusion of a fraction BCH-N-A as the outlier. After that, the remaining fractions of BCH-N revealed even the statistically significant correlation between fraction size and content of substituted naphthalenes and N- and S- substituted heterocycles.

A similar relationship between biochar particle size and the content of PAHs and heterocyclic compounds was also observed by the authors of publications [54]. In our presented results, the differences between the individual biochar size fractions were less pronounced, which can be attributed to the smaller size fractions used in our experiments. Moreover, the comparison between the individual biochar samples reflected the slightly higher content of all the detected groups of aromatic organic compounds in the fractions of BCH-N followed by BCH-S. Only in the case of S-substituted heterocyclic compounds, the order was BCH-N, followed by fractions of BCH-CZ. These observed dependences of the content of polycyclic aromatic structures detected in the individual fractions of biochar samples follow trends in W_{ORG} determined by the thermogravimetry (Table 4). 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 according to the literature [22,30] connected with the variations in pyrolysis conditions and partially also with the differences in used biomass feedstock. As was 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 [31,48] describes HMW PAHs as a more serious issue, as they exhibit significantly higher toxicity compared to LHMW PAHs. The formation of the individual PAHs is summarized in the reviews [30,31,48,53]. The data shown in Figure 5 indicate the direct connection of the relative content of HMW PAHs (compared to the LMW PHAs) with the used pyrolysis temperature. It is visible from Figure 5 that the contents of HMW PHAs (containing 4, 5 and 6 cycles) are more pronounced for fractions of the BCH-N sample (produced at 720 °C) compared to the BCH-CZ (produced at 450–470 °C). Our results are in good agreement with the data published by other authors [31,53].

Table 8. 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*	-0.280	-0.913	-0.918	-0.756
BCH-CZ*	indirect	indirect	indirect	indirect

* data with excluded fraction BCH-N-A.

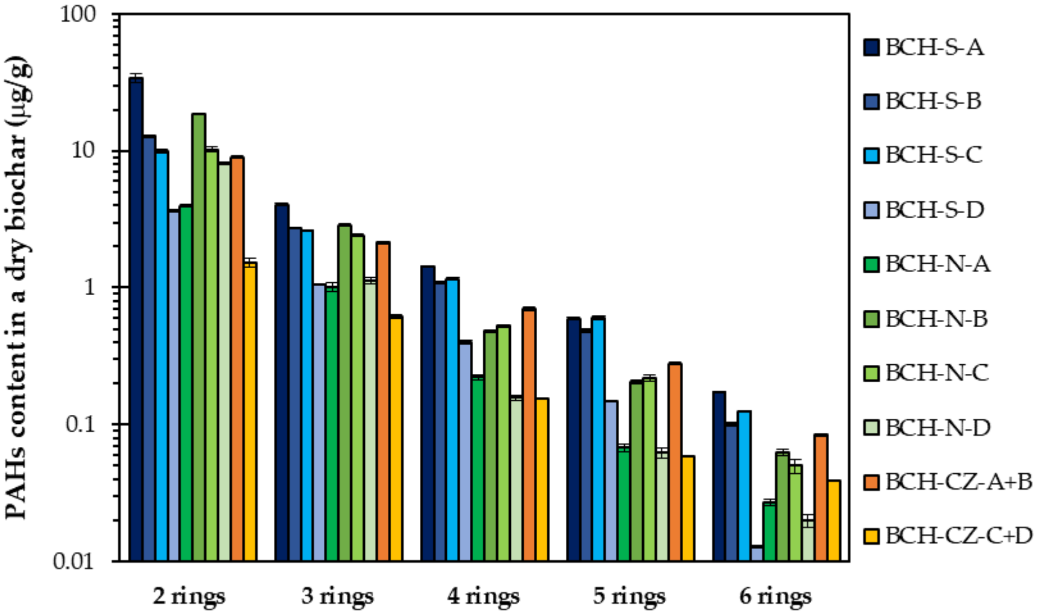

Figure 5. GC–MS characterization of the effect of biochar size fraction on the content of different types of polyaromatic compounds (based on the number of aromatic rings in structure).

Among the quantified compounds, naphthalene and alkyl-substituted naphthalene structures also significantly exceed all other studied compounds in their detected concentration, which were orders of magnitude higher. Nevertheless, these analytes are in the vast majority, they are 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 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, but also 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 defence mechanisms against herbivores, nutrient uptake and overall plant productivity can be mentioned. However, VOCs also affect soil microorganisms [31]. Indeed, these effects are not long-lasting because they are not capable of persistence in soil and quickly decompose, which is related to their release from the soil into the atmosphere [55].

3.3. Multivariate statistical characterization of biochars

The results of the particular analyses (discussed in sections 3.1. and 3.2.) were also further processed by the principal component analysis using Statistica software (Tibco Software Inc.). Factor loadings plot and projection of observation on the plane of principal components are presented in Figure 6. Biochar samples are projected onto the plane 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. PCA plot revealed a clear separation of three biochar types corresponding to the three independent purchased samples. For this reason, the most crucial aspen driving biochar properties were the producers' dependent parameters e.g. used biomass feedstock, pyrolysis conditions, used pre-treatments before the pyrolysis etc.

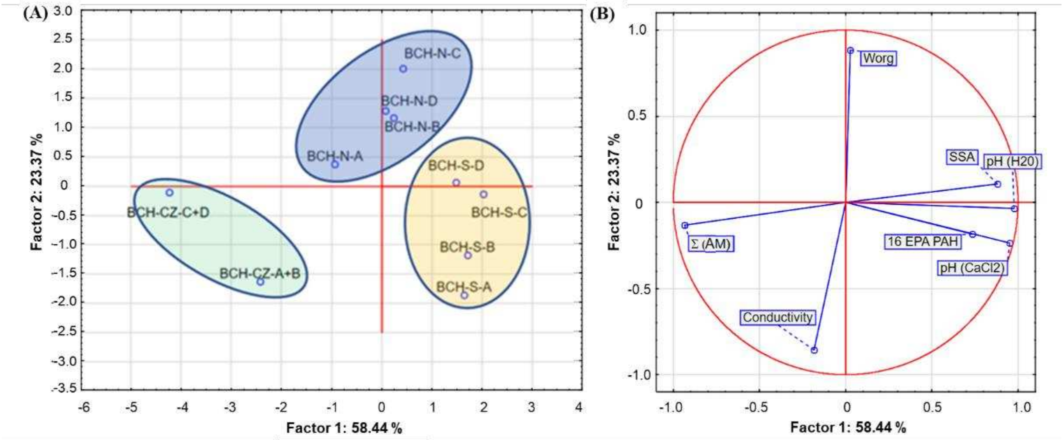

Figure 6. Projection of the observation scores (A) and variables (B) into factor plane of principal components F1 and F2.

PCA analysis at the same time also revealed the effect of biochar fraction size on the chemical and physical properties of studied samples. With increasing particle size, there is 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 reflected slightly lower total aqueous extractable content of $\Sigma_{(AM)}$(sum of alkaline metals and alkaline Earth metals) and lower extraction efficiency of 16 EPA PAHs.

4. Conclusions

The agronomical utilization of biochar as a soil supplement is recently increasing in popularity, even though some areas of its research still lack in-depth research. The results of our research have shown that the most crucial parameters affecting biochar properties were the production source feedstock material and production conditions. Besides these producer-dependent parameters, the size fraction of biochar together with its specific surface area also influences the physicochemical properties of the material and its potential to leach the 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 studied biochar samples (BCH-N, BCH-S and BCH-CZ). The comparison of the total detected content of K in the biochar samples (5–25 mg/g) with the aqueous extractable contents (1–6 mg/g) indicates the potential to be accessed repeatedly after the application to the soil. The initial aqueous leaching of biochar in soil (by water from rain or irrigation) provides a slightly alkaline pH response. Besides K, the attention was focused also on the content and availability of remaining macroelements (Na, Ca, Mg and P) and microelements (Al, Fe, Zn, Mn, Cu, Cr, Ni). These mineral components were detected in aqueous extracts of all the studied fractions of biochar samples. Generally, the highest contents of the aqueous-extractable macroelements were detected in leachates of BCH-CZ. Fractions of this biochar reflected the lowest pH, which probably induced the solubility of some insoluble mineral components present in biochar. We have identified a statistically significant indirect relation between the 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. The detected contents of aqueous-extractable micronutrients were compared to macronutrients almost three orders lower (in the range of μg/g). The total detected contents of microelements again indicated the potential of biochar to release these types of elements from its structure gradually in a longer time scale. The modern way of land tillage and cultivation practices creates increased demands for the availability of soil micronutrients, nevertheless, their common concentration in soils is extremely low (units to dozens of ppm). The effect of biochar fraction size was not consistent for all the measured microelements. The increase in the size of the fraction resulted in a decrease in the aqueous-extractable Fe and Zn and oppositely in an increase in extractable Al.

The attention of our research was focused also 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. The comparison with physicochemical characterization indicates the direct relation of polycyclic aromatic structure content with the total content of organic matter in biochar samples and a statistically significant indirect relation to the particle size for BCH-S and BCH-CZ biochar samples and after the exclusion of the finest fraction BCH-N-A also for the sample of BCH-N.

In conclusion, the finer fractions of biochar samples according to our results provided higher amounts of aqueous-extractable macro- and microelements, which can be further repeatedly released to the surrounding soil. The comparison of individual biochar samples showed that the middle-sized fractions (0.5–2 and 2–4 mm) of BCH-S were the most promising considering the potential agronomical application as they reflected well-developed internal porous structure, appropriate physico-chemical conditions (pH, conductivity), PAHs content far below the limits, approximately 60 wt.% of organic carbon and a high content of available macro- and microelements. When applied as a soil conditioner, the mineral contents of biochar can be gradually released. This provides the necessary macro- and microelements for the plants in the soil, which is besides the other well-known positive effects of biochar on soil properties, an important conclusion. We believe the results summarized in our work will provide necessary insight into the description of biochar mineral content, its connection to biochar texture, corresponding physicochemical properties and potential availability to leach nutrients to the soil. These findings could help in further assessment of biochar utilization in modern agriculture as a soil conditioner.

Author Contributions: Conceptualization, M.K.; methodology, M.K, J.P and L.M; investigation, S.S, J.P., L.M. and L.K.; writing—original draft preparation, M.K., S.S., J.S., and L.M.; writing—review and editing, M.K., J.S., J.P., and L.M.; supervision, M.K.; project administration, M.K.; funding acquisition, M.K. All authors have read and agreed to the published version of the manuscript.

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