Article

Is It Possible to Control the Nutrient Regime of Soils with Different Texture through Biochar Substrates?

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Abstract: Understanding nutrient management is essential to ensure healthy and adequate food production, especially in the context of biochar applied to soil with different soil textures. Additionally, farmers are beginning to understand the importance of nutrient management and there are still several knowledge gaps in this area. Several studies on biochar showed its positive effects, especially in sandy and nutrient-poor soils. There is still a lack of information on the impact of biochar on nutrient regimes in texturally different soils with sufficient nutrient supply and favorable soil chemistry. This study investigates the effect of two biochar substrates (a) biochar blended with farmyard manure (BS1), and (b) biochar blended with farmyard manure and digestate (BS2) applied at rates of 10 and 20 t ha⁻¹ alone or in combination with fertilization on the changes in sorption capacity and nutrient regime of two texturally different soils: (a) sandy Arenosol, and (b) loamy Chernozem, (both in western Slovakia) which have a favorable nutrient content. The results showed that in sandy soil, the BS2 at rate of 20 t ha⁻¹ increased the sum of basic cations (by +112%) and CEC (by +93%) compared to the control. In sandy soil, the content of total P increased by +35 and +16% in BS1 20 t ha⁻¹ and BS2 20 t ha⁻¹, respectively, when compared to the unfertilized control. The content of total P increased by +18% in BS1 20 t ha⁻¹ after fertilization compared to the fertilized control. In loamy soil, the content of total P increased significantly by +53 and +14% in unfertilized treatment BS2 20 t ha⁻¹ and fertilized treatment with BS1 at 20 t ha⁻¹ compared to the respective controls. Available Ca increased in sandy soil by +50 and +53% in fertilized treatments with BS2 at 20 t ha⁻¹ and BS1 at 20 t ha⁻¹, respectively, when compared to fertilized control. In loamy soil, available Mg increased by +13% in fertilized treatment with BS1 applied at 20 t ha⁻¹. In conclusion, BS application at a dose of 20 t ha⁻¹ had a stronger positive effect on soil sorption parameters in sandy soil than the application dose of 10 t ha⁻¹. The same BS application rate significantly increased total P in both soils.

Keywords: soil sorption; soil reaction; fertilizer amendment; available nutrients; *effeco*

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1. Introduction

Monitoring of the chemical soil parameters is an integral part of modern agricultural practice. It acts as a tool to evaluate the potential of soil to provide ecosystem services such as regulation of nutrients and uptake and food, fuel, and energy production. A frequent assessment of the soil properties is an important indicator for soil management. Based on the content of individual nutrients, the farmers can determine how to implement rational fertilization, which has positive economic and environmental impacts on their farming system. The content of nutrients in the soil is determined by local conditions (parent material, soil texture, weathering processes, climate, etc.), but they can be significantly controlled by planned intervention, particularly fertilization. Since 2000, OECD countries have on average experienced declining trends in nutrient surpluses. Although almost all OECD countries recorded a decrease in phosphorus surpluses, the picture is mixed in

the case of nitrogen due to increased nitrogen fertilizer application rates. From 1992 to 2014, the average nitrogen surplus fell from 85 kg ha⁻¹ to 67 kg ha⁻¹ and the phosphorus surplus from 13 kg ha⁻¹ to 6 kg ha⁻¹ in OECD countries. Up to 1990, the average NPK annual doses to arable soil were 220–230 kg ha⁻¹ in Slovakia. Since that period, the doses of NPK fertilizers dropped significantly to 40–60 kg ha⁻¹ (especially due to economic reasons). Currently, the nutrient doses are at the level of 100 kg ha⁻¹ NPK—nitrogen is generally the most applied fertilizer (76.31 kg ha⁻¹), followed by significantly less amount of phosphorus (14.45 kg ha⁻¹) and potassium (11 kg ha⁻¹). The content of soil nutrients has been regularly monitored since 1956, partially because of the introduction of the soil agrochemical testing (SAT), and a Partial Monitoring System of Soil as a part of the Environmental Monitoring of Slovakia [1]. The results of SAT in Slovakia (from 1956 up to the present day) show that the content of available phosphorus in Slovak soils gradually increased due to intensive phosphorus fertilization until the 1990s. However, the phosphorus fertilization was insufficient and at a lower level than the uptake of phosphorus from the soil by crops. Therefore, the content of available phosphorus is currently at a level comparable to the 1970's. In many cases, the phosphorus in the soil becomes a limiting factor for crop yield and soil quality. This negative trend is also supported by increasing acidity of the soil leading to chemical sorption of phosphorus, and thus a reduction in the availability of phosphorus to plants [2]. In the agricultural soils of Slovakia, the content of available potassium is ranging relatively widely, on average from 121–401 mg kg⁻¹, which represents a “low” up to “very high” supply of potassium (K) to the soils. Since 1993, the K content has decreased on average by 20–25% [1]. On the other hand, the content of total Ca is within the range of 0.15–6.0%. Annually, approximately 30 kg of Ca ha⁻¹ is received through the application of manures and composts. Most Ca (approximately 157 kg ha⁻¹) is added through liming of acidic soils [3], but losses through leaching and uptake by crops can represent 50–600 kg kg⁻¹ and 125–400 kg kg⁻¹, respectively [4,5]. The content of total Mg ranges from 0.4% to 0.6%. Available Mg content of 95% of Slovak soils is between “satisfactory” up to “very high” content. Despite this fact, Kováčik [6] stated that Mg losses can be in the range from 50–80 kg ha⁻¹.

In the case of some macro-nutrients, there is a continuous significant reduction in their content in the soils of the Slovak Republic. It is the responsibility of farmers to supplement the missing nutrients to the soil through the addition of fertilizers. Generally, the application of mineral fertilizers is the fastest way to increase the nutrient content in the soil for crops in terms of time and efficiency, and their application has increased significantly in recent decades [7]. But fertilization as an agronomic tool of modern agriculture also has some disadvantages—especially its incorrect utilization. The effect of mineral fertilization improves when it is combined with an organic amendment. In such cases, the negative aspects of its application (a reduction of physical properties, acidification, salinization, etc.) can be eliminated. Recently, a pyrolyzed organic soil amendment—biochar and its various combinations with other fertilizers have been used in many regions of the world to sustainably increase the nutrient reserves in the soil. Biochar is a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment. Several authors [5,8] reported that applied biochar improved soil quality by increasing soil pH as a result of a soil acidity reduction—known as the liming effect [9]. This leads to the improvement of cation exchangeability and nutrient preservation within the soil. The application of biochar improves soil fertility through two mechanisms: (1.) adding the nutrients to the soil and/or (2.) retaining the nutrients from other sources, including nutrients from the soil itself. As some authors e.g., [10] have mentioned, biochar serves as an important source of plant nutrients, especially nitrogen in biochar produced from manures and wastes at low temperatures (<400 °C). However, the phosphorus, potassium, and other nutrient contents are generally higher in manure/waste biochars than in biochars made of wood or crop residues. Biochar increases the availability of N, Ca, Mg, K, P to the plants, because biochar adsorbs and slowly releases fertilizers [11]. In the case of crops with high nutrient requirements, the application of biochar alone is not always a

sufficient source to cover nutrient requirements for crop growth and soil productivity. But the application of biochar in combination with other fertilizers or the production of the innovative biochar substrates (BS) can be an effective way to meet the increasing nutrient requirements in intensive agriculture [12]. However, it is important for farmers to know whether a product such as BS brings them benefits through increased yields, improved soil properties, and net economic profit [13]. As biochar is expected to be the unbalanced fertilizer due to its high stability in the soil environment, its addition to the soil may play a key role in nutrient dynamics by directly adding or indirectly affecting the soil properties that increase nutrient availability [10,11,14]. Therefore, biochar producers must strive in the process of their production to achieve a product with the most optimal properties or recommend its application with other fertilizers in various combinations [15,16].

The application of biochar and its effect on the soil properties both in Slovakia and globally is not fully understood and requires further research. Published literature presents several examples [17,18] that biochar improves soil fertility, including nutrient regime and soil pH in coarse and acidic soils rather than in fine soils and soils rich in nutrients with alkaline pH. However, with farmer intervention, even coarse-textured soils can have higher pH and a good supply of nutrients. In many cases, the content of nutrients in biochar is highly unbalanced as its properties depend on the feedstock, the conditions of biochar production, etc. [19]. This effect can be eliminated by combining biochar with other soil amendments/fertilizers, especially by providing additional nutrients. Many questions arise here. How will be soils that have an alkaline reaction and a good supply of nutrients, but a different soil texture affected by the application of biochar substrates (BS)? How will texturally different soils react to different doses of BS and their combinations with other fertilizers? In our study, we hypothesized that overall, more positive changes will be observed in the treatments with an addition of fertilizers to BS and that a more pronounced effect will be observed at higher application rates of BS. It was assumed that nutrients contained in applied BS will improve the sorption capacity of sandy soil more than of loamy soil [20,21] and that after the addition of BS, the availability of nutrients to plants will decrease. The aims of this study were (1.) to quantify the total and available nutrient contents in texturally different soils after the application of the biochar substrates alone or in combination with additional fertilization, (2.) to determine whether there are direct relationships between pH, sorption and macro-nutrients in the BS amended treatments in the texturally different soils.

2. Materials and Methods

2.1. Experimental Sites and Research Design

The study was conducted in two research sites at Dolná Streda (48°15'16.6" N 17°43'02.7" E) and Veľké Úľany (48°09'11.5" N 17°34'57.6" E), both located in western Slovakia. The climate is temperate with an average annual temperature ranging from 9–10 °C and the average annual rainfall ranges from 520–600 mm in both regions. The soils at Dolná Streda and Veľké Úľany are classified as the sandy Haplic Arenosol (Arenic, Calcic) and the loamy Vermic Chernozem (Mollic, Loamic), respectively [22]. The physical and chemical soil characteristics determined before the experiment are listed in Table 1.

Biochar substrates (BS) used in the experiment were provided by Zdroje Zeme a. s. (Slovakia). According to the manufacturer, biochar was made from pyrolyzed hardwood and blended with other organic amendments. Biochar substrate 1 (BS1) was mixed with dried sheep manure in the ratio 1:1 and biochar substrate 2 (BS2) was mixed with dried sheep manure and the residue (digestate) from the biogas plant (cattle manure as feedstock) in the ratio 1:1:1. The selected characteristics of BS sold under trademark “*effeco*” are summarized in Table 2.

Table 1. The basic chemical and physical properties of soil before the establishment of the experiments.

Soil Property	Dolná Streda Sandy Haplic Arenosol (Arenic, Calcic)	Veľké Úľany Loamy Vermic Chernozem (Mollic, Loamic)
Sand (%)	81.9	38.5
Silt (%)	10.5	47.8
Clay (%)	7.60	13.7
OC (g kg ⁻¹)	9.70	15.6
Total N (mg kg ⁻¹)	1300	1000
Available P (mg kg ⁻¹)	175	129
Available K (mg kg ⁻¹)	165	255
pH	7.60	7.78

OC—organic carbon in the soil.

Table 2. The basic chemical and physical properties of the used biochar substrates BS1 and BS2.

	BS1	BS2
Pellets (dimensions in mm)	2 · 2 · 1	2 · 2 · 1
OC (%)	43	45.4
Total N (%)	1.20	1.30
Total P (%)	0.49	0.79
Total K (%)	24.6	15.5
pH	8.18	8.44
Total Ca (mg kg ⁻¹)	42,000	22,000
Total Mg (mg kg ⁻¹)	4500	5800

OC—organic carbon in the biochar substrates.

Detailed information on the experimental design can be found in the work of Šrank and Šimanský [23]. Briefly, the experiment in Dolná Streda was established using the long segment method in autumn 2017 on 10 plots (one treatment = 90 m²). The research plots were planted with sunflower (*Helianthus annuus* L.), durum wheat (*Triticum durum* Desf.), and maize (*Zea mays* L.) in 2018, 2019, and 2020, respectively. Eight biochar amended treatments (BS1 10 t ha⁻¹, BS1 20 t ha⁻¹, BS2 10 t ha⁻¹, BS2 20 t ha⁻¹, BS1 10 t ha⁻¹ + F, BS1 20 t ha⁻¹ + F, BS2 10 t ha⁻¹ + F, and BS2 20 t ha⁻¹ + F) and two control treatments (Co: control—no fertilization and no biochar, Co-F: fertilized control with no biochar) were investigated in 3 replicates. Biochar substrates BS1 and BS2 were applied in autumn 2017 and incorporated into the soil by disk harrow. During the whole period of the experiment, the site was under minimum tillage management. Only disc harrow operations were performed up to a depth of 15–18 cm. Before sowing sunflower in spring 2018, urea was applied to the soil at a dose of 100 kg ha⁻¹. In autumn 2018 and spring 2019, urea and monoammonium phosphate (AMOFOS NP 12–52) were applied at the rates of 100 kg ha⁻¹ and 100 kg ha⁻¹, respectively. The same fertilizers and the same application doses were used with maize in 2020.

The experiment in Veľké Úľany was established using a random plot arrangement method with double repetition in spring 2018 with a total of 10 treatments (one treatment = 25 m²). The preceding crop was carrot (*Daucus sativus* Hoffm.). Green pepper (*Capsicum annuum* L.), beetroot (*Beta vulgaris* L.) and green pepper were planted in 2018, 2019, and 2020, respectively. Similarly to the experiment in Dolná Streda, the experiment consisted of the same eight treatments: Co: control without fertilization, BS1 10 t ha⁻¹, BS1 20 t ha⁻¹, BS2 10 t ha⁻¹, BS2 20 t ha⁻¹, Co-F as fertilized control, BS1 10 t ha⁻¹ + F, BS1 20 t ha⁻¹ + F, BS2 10 t ha⁻¹ + F and BS2 20 t ha⁻¹ + F. Biochar substrates BS1 and BS2 were incorporated into the soil at a depth of 10–12 cm together with granulated manure Italtollina at the rate of 0.85 t ha⁻¹ before planting green pepper in 2018. Italtollina was applied once again at a rate of 1 t ha⁻¹ before planting the beetroot in spring 2019. In spring 2020, NPK fertilizer at the rate of 200 kg ha⁻¹ was applied and incorporated into the soil before planting green pepper. Conventional tillage practices were applied at the site during the experiment. The

soil was always tilled in autumn to a depth of 20 cm. In spring, the soil was consequently prepared by a tiller. Depending on the type of grown vegetable, mechanical hoeing was also used in combination with the chemical weed control.

2.2. Soil Analyzes

The soil samples were taken from all treatments of both experiments twice a year (in spring and autumn) during the period from 2018–2020 from a depth of 0–20 cm. Samples were measured for: soil pH—potentiometrically; sorption parameters such as: hydrolytic acidity (Ha)—titration in the extract of $1 \text{ mol dm}^{-3} \text{ CH}_3\text{COONa}$, sum of basic cations (SBC)—titration in leachate of $1 \text{ mol dm}^{-3} \text{ HCl}$ —Kappen method [24]. In the final samples, the values of cation exchange capacity (CEC) were calculated according to Equation (1).

$$\text{CEC} = \text{Ha} + \text{SBC}, \quad (1)$$

Base saturation (Bs) of the soil colloidal sorption complex was calculated according to Equation (2).

$$\text{Bs} = \text{SBC} / \text{CEC} \cdot 100, \quad (2)$$

Total contents of K, Ca, and Mg were determined by flame atomic absorption spectrometry (Perkin Elmer AA 2100) and the content of total P by the molybdenum–blue method after samples were incorporated into a mixture of HF, HClO₄, and HNO₃ in a ratio of 3:1:1 by volume. Available forms of the investigated elements were measured by flame atomic absorption spectrometry (Perkin Elmer AA 2100) and the content of available P was estimated by the molybdenum–blue method after sample extraction in Mehlich III solution [25].

2.3. Statistical Analyzes

The statistical analyzes were performed using the Statgraphics Centurion XV.I programme (Statpoint Technologies, Inc., Washington, DC, USA). One-way analysis of variance (ANOVA) and the least significant difference (LSD) method were used to compare treatment means for the two types and levels of biochar substrates application and their combination with other fertilization at $p \leq 0.05$. To study the relationships between the soil pH, sorption parameters, and available forms of P, K, Ca, and Mg, a single linear regression analysis was applied.

3. Results and Discussion

The findings in this study confirmed that the application of different types of biochar substrates (BS) to different soils affected the evaluated soil properties. The soil pH and soil sorption parameters of unfertilized soils and at treatments with BS after 3 years of experiments are listed in Table 3. In sandy soil, the overall average pH values ranged from 7.41 to 7.63, i.e., from neutral to slightly alkaline. In the case of BS2 treatments (BS2 10 t ha^{−1} and BS2 20 t ha^{−1}), the soil pH values significantly increased (both by +3%) after the application of BS to the soil compared to the unfertilized control Co. However, the combination of BS together with additional fertilization had no effect on average pH in sandy soil compared to the fertilized control for the period 2018–2020. In loamy soil, the pH was within the range of 7.83–8.03, and the application of BS did not alter the observed average soil pH. Our results are consistent with the published results of several studies [21,26–29]. El-Naggar, et al. [21] stated that a more pronounced effect of biochar on soil pH changes was usually observed in sandy soils and in soils with acidic pH than in soils with finer texture. Overall, the soil pH values in our study were lower in sandy soil. A general slightly higher increase in sandy soil pH compared to loamy soil may be a result of the initial pH of both soils. In addition, both soils contained carbonates, and both tested BS contained basic cations and had an alkaline pH. In general, by increasing soil pH, biochar positively affected an increase of cation exchange capacity of the soil (CEC). An increase in soil pH increases the electrostatic bonds between the soil particles and exchange

cations, as well as increases the overall sorption capacity [30]. In our study, the effect of BS on soil pH was different depending mainly on the soil type/class, but also on the type of BS and its application rate or combination with additional fertilization. A stronger effect was observed in sandy soil, which corresponds to the observed average values of sorption parameters in both trials (Table 3).

Table 3. Parameters of the soil sorption complex (mean $\pm$ standard deviation for 2018–2020).

Treatments	pH	Ha	SBC	CEC	Bs
		mmol kg ⁻¹	mmol kg ⁻¹	mmol kg ⁻¹	%
Sandy soil					
Co	7.41 ± 0.19 ^a	3.29 ± 0.49 ^a	19.7 ± 5.85 ^a	23.0 ± 6.10 ^a	81.3 ± 1.30 ^a
BS1 10 t ha ⁻¹	7.57 ± 0.16 ^{ab}	3.19 ± 1.22 ^a	24.8 ± 7.20 ^{ab}	28.0 ± 7.30 ^{ab}	88.3 ± 5.13 ^{ab}
BS1 20 t ha ⁻¹	7.53 ± 0.14 ^{ab}	2.94 ± 0.78 ^a	34.1 ± 8.12 ^{ab}	37.0 ± 8.13 ^{ab}	91.7 ± 1.27 ^b
BS2 10 t ha ⁻¹	7.63 ± 0.20 ^b	2.57 ± 0.41 ^a	28.7 ± 8.10 ^{ab}	31.3 ± 9.11 ^{ab}	91.1 ± 2.47 ^{ab}
BS2 20 t ha ⁻¹	7.63 ± 0.12 ^b	2.80 ± 0.45 ^a	41.9 ± 7.10 ^b	44.6 ± 7.98 ^b	92.9 ± 2.15 ^b
Co-F	7.51 ± 0.20 ^a	3.35 ± 0.44 ^a	46.5 ± 8.75 ^{bc}	49.8 ± 9.90 ^{bc}	92.1 ± 3.79 ^a
BS1 10 t ha ⁻¹ + F	7.59 ± 0.22 ^a	3.00 ± 1.34 ^a	29.6 ± 5.61 ^{ab}	32.5 ± 1.00 ^{ab}	91.0 ± 2.46 ^a
BS1 20 t ha ⁻¹ + F	7.58 ± 0.12 ^a	3.64 ± 1.75 ^a	57.4 ± 5.33 ^c	61.0 ± 6.13 ^c	93.9 ± 2.84 ^a
BS2 10 t ha ⁻¹ + F	7.45 ± 0.26 ^a	3.38 ± 2.00 ^a	25.6 ± 5.45 ^a	29.0 ± 5.34 ^a	87.3 ± 3.39 ^a
BS2 20 t ha ⁻¹ + F	7.63 ± 0.10 ^a	3.19 ± 1.22 ^a	34.8 ± 1.09 ^{ab}	38.0 ± 2.31 ^{ab}	91.7 ± 2.72 ^a
Loamy soil					
Co	7.83 ± 0.21 ^a	3.14 ± 1.48 ^a	492.6 ± 1.48 ^a	495.8 ± 2.98 ^a	99.4 ± 0.30 ^a
BS1 10 t ha ⁻¹	8.03 ± 0.14 ^a	3.01 ± 1.50 ^a	490.8 ± 2.47 ^a	493.9 ± 2.69 ^a	99.4 ± 0.30 ^a
BS1 20 t ha ⁻¹	8.00 ± 0.13 ^a	2.55 ± 1.25 ^a	491.3 ± 2.82 ^a	493.8 ± 2.67 ^a	99.5 ± 0.25 ^a
BS2 10 t ha ⁻¹	7.97 ± 0.16 ^a	2.60 ± 1.23 ^a	491.8 ± 4.37 ^a	494.4 ± 2.46 ^a	99.5 ± 0.25 ^a
BS2 20 t ha ⁻¹	7.91 ± 0.15 ^a	2.88 ± 1.16 ^a	492.2 ± 3.82 ^a	495.4 ± 3.23 ^a	99.4 ± 0.23 ^a
Co-F	7.99 ± 0.14 ^a	2.58 ± 0.92 ^a	492.4 ± 2.94 ^a	495.0 ± 2.07 ^a	99.5 ± 0.19 ^a
BS1 10 t ha ⁻¹ + F	7.91 ± 0.16 ^a	2.78 ± 1.42 ^a	492.7 ± 2.57 ^a	495.5 ± 2.64 ^a	99.4 ± 0.30 ^a
BS1 20 t ha ⁻¹ + F	7.98 ± 0.12 ^a	2.91 ± 1.38 ^a	492.7 ± 2.34 ^a	495.6 ± 2.36 ^a	99.5 ± 0.29 ^a
BS2 10 t ha ⁻¹ + F	8.00 ± 0.17 ^a	2.60 ± 1.18 ^a	493.4 ± 2.18 ^a	496.0 ± 2.05 ^a	99.5 ± 0.24 ^a
BS2 20 t ha ⁻¹ + F	7.98 ± 0.16 ^a	2.85 ± 1.17 ^a	492.4 ± 2.61 ^a	495.3 ± 2.49 ^a	99.4 ± 0.24 ^a

Ha—Hydrolytic acidity; SBC—Sum of basic cations; CEC—Cation exchange capacity; Bs—Base saturation. Different letters between the individual treatments stand for a significant difference according to the LSD test ($p < 0.05$).

The average values of hydrolytic acidity (Ha) did not significantly change in any of the studied soils for the period of 3 years after the application of BS (Table 3). Regarding the sum of basic cations (SBC), in sandy soil, its values increased on average by +26, +73, +46, and +112% in treatments BS1 10 t ha⁻¹, BS1 20 t ha⁻¹, BS2 10 t ha⁻¹, and BS2 20 t ha⁻¹, respectively (Table 3). The effect was more pronounced at the higher application rate of BS. SBC increase after BS incorporation into the soil could be due to providing basic cations that were formed in BS during the process of production (pyrolysis) [31]. Conversely, SBC decreased (except for treatment BS1 20 t ha⁻¹ + F) by −36, −45, and −25% in treatments BS1 10 t ha⁻¹ + F, BS2 10 t ha⁻¹ + F, and BS2 20 t ha⁻¹ + F, respectively after application of BS together with additional fertilization compared to fertilized control. However, the significant changes of SBS were observed only in treatment BS2 10 t ha⁻¹ + F. In loamy soil, the application of BS did not have any effect on SBC.

CEC reflected the trend in the values of Ha and SBC, i.e., an increase in CEC after BS application compared to unfertilized control (with stronger effect at BS2 and higher application rate of both BS), but also a decrease in average values of CEC in BS combined with additional fertilization (except for treatment BS1 20 t ha⁻¹ + F) compared to the fertilized control. Significant differences were observed only in sandy soil for treatment BS2 20 t ha⁻¹ (+93%) and BS2 10 t ha⁻¹ + F (−42%) compared to their control treatments Co and Co-F, respectively (Table 3). In loamy soil, the differences between unfertilized and fertilized treatments were not significant. This can be explained as follows: in sandy soil, there are more favorable conditions for the oxidation of biochar, which contains carboxyl groups on its surface [32]. Carboxyl groups can also have a significant neutralizing effect [33], which resulted in a decrease in Ha, but also an increase in SBC and CEC.

Application of BS significantly increased base saturation (Bs) by +13 and +14% only in sandy soil in treatments with an application rate of 20 t ha⁻¹ of both biochar substrates (BS1 20 t ha⁻¹ and BS2 20 t ha⁻¹, respectively) without fertilization. The application of BS with additional fertilization in sandy soil, nor any application of BS in loamy soil did not have a significant effect on changes in Bs, probably as a result of saturation of sorption complex with basic cations in both soils (in loamy soil, the sorption complex was even fully saturated >95%).

The content of total P in the soil generally depends on its content in the parent material and the soil organic matter [3], but also on its content in the fertilizer/additives applied to the soil. The content of P in biochar mainly depends on the P content in the feedstock and the conditions of biochar production [10]. The biochar substrates BS1 and BS2 contained 0.49% and 0.79% of phosphorus, respectively. It was expected that BS incorporation will have a positive effect on the overall increase in P content in both soils. In sandy soil, the content of total P increased by +12, +35, +2, and +16% in treatments BS1 10 t ha⁻¹, BS1 20 t ha⁻¹, BS2 10 t ha⁻¹, and BS2 20 t ha⁻¹, respectively, compared to the unfertilized control (Table 4).

Table 4. Contents of total and available macro-nutrients (mean ± standard deviation for 2018–2020).

Treatment	Total Content (g kg ⁻¹)				Available Content (mg kg ⁻¹)			
	P	K	Ca	Mg	P	K	Ca	Mg
Sandy soil								
Co	1.15 ± 0.15 ^a	11.2 ± 0.34 ^a	40.2 ± 1.33 ^a	9.52 ± 0.99 ^a	374 ± 65 ^a	166 ± 78 ^a	7362 ± 1376 ^a	255 ± 28 ^a
BS1 10 t ha ⁻¹	1.29 ± 0.11 ^a	11.5 ± 0.28 ^a	40.9 ± 0.99 ^a	9.85 ± 1.12 ^a	359 ± 39 ^a	226 ± 35 ^a	6758 ± 2987 ^a	231 ± 41 ^a
BS1 20 t ha ⁻¹	1.55 ± 0.08 ^c	12.4 ± 0.36 ^a	33.5 ± 6.89 ^a	8.82 ± 2.53 ^a	370 ± 26 ^a	239 ± 22 ^a	5842 ± 2907 ^a	285 ± 36 ^a
BS2 10 t ha ⁻¹	1.17 ± 0.07 ^a	11.3 ± 0.41 ^a	34.4 ± 5.99 ^a	7.99 ± 1.99 ^a	336 ± 59 ^a	174 ± 41 ^a	5803 ± 2699 ^a	250 ± 26 ^a
BS2 20 t ha ⁻¹	1.34 ± 0.11 ^b	11.8 ± 0.09 ^a	31.1 ± 10.3 ^a	7.36 ± 2.37 ^a	396 ± 19 ^a	215 ± 59 ^a	5371 ± 2639 ^a	275 ± 39 ^a
Co-F	1.06 ± 0.05 ^a	11.5 ± 0.23 ^a	29.8 ± 9.87 ^a	7.23 ± 3.07 ^a	329 ± 44 ^a	200 ± 28 ^a	5773 ± 1563 ^a	280 ± 55 ^a
BS1 10 t ha ⁻¹ + F	1.12 ± 0.03 ^{ab}	11.2 ± 0.35 ^a	39.4 ± 5.89 ^a	9.50 ± 2.87 ^a	290 ± 39 ^a	197 ± 37 ^a	5927 ± 1302 ^a	294 ± 37 ^a
BS1 20 t ha ⁻¹ + F	1.25 ± 0.11 ^b	11.6 ± 0.42 ^a	32.0 ± 11.4 ^a	7.92 ± 2.99 ^a	362 ± 48 ^a	213 ± 35 ^a	8854 ± 2744 ^b	281 ± 22 ^a
BS2 10 t ha ⁻¹ + F	1.09 ± 0.04 ^a	11.7 ± 0.28 ^a	32.9 ± 8.34 ^a	8.50 ± 1.89 ^a	321 ± 62 ^a	228 ± 21 ^a	7333 ± 974 ^{ab}	310 ± 49 ^a
BS2 20 t ha ⁻¹ + F	1.16 ± 0.06 ^{ab}	11.7 ± 0.36 ^a	36.9 ± 3.29 ^a	9.11 ± 2.75 ^a	297 ± 28 ^a	263 ± 18 ^b	8675 ± 1693 ^b	301 ± 38 ^a
Loamy soil								
Co	1.01 ± 0.08 ^a	14.1 ± 0.44 ^a	42.3 ± 5.67 ^a	14.9 ± 1.21 ^a	166 ± 48 ^a	215 ± 36 ^a	9156 ± 896 ^{ab}	371 ± 11 ^a
BS1 10 t ha ⁻¹	1.11 ± 0.09 ^{ab}	14.6 ± 0.24 ^a	47.9 ± 4.79 ^a	16.5 ± 0.33 ^b	126 ± 59 ^a	199 ± 28 ^a	9834 ± 751 ^b	366 ± 19 ^a
BS1 20 t ha ⁻¹	1.16 ± 0.10 ^{ab}	14.6 ± 0.31 ^a	49.7 ± 3.99 ^a	19.6 ± 1.11 ^c	147 ± 36 ^a	227 ± 39 ^a	8967 ± 879 ^{ab}	386 ± 20 ^a
BS2 10 t ha ⁻¹	1.20 ± 0.11 ^{ab}	14.5 ± 0.15 ^a	45.0 ± 4.56 ^a	16.0 ± 0.46 ^{ab}	159 ± 29 ^a	207 ± 26 ^a	8618 ± 235 ^a	393 ± 26 ^a
BS2 20 t ha ⁻¹	1.54 ± 0.21 ^b	14.5 ± 0.09 ^a	45.6 ± 3.87 ^a	16.4 ± 0.49 ^b	149 ± 37 ^a	208 ± 37 ^a	8334 ± 649 ^a	380 ± 17 ^a
Co-F	1.07 ± 0.04 ^a	14.9 ± 0.12 ^a	45.8 ± 1.23 ^a	17.3 ± 0.12 ^a	141 ± 33 ^a	191 ± 68 ^a	9875 ± 976 ^a	386 ± 05 ^a
BS1 10 t ha ⁻¹ + F	1.09 ± 0.04 ^a	14.8 ± 0.22 ^a	43.5 ± 4.35 ^a	17.0 ± 0.45 ^a	166 ± 28 ^a	289 ± 73 ^a	8125 ± 959 ^a	389 ± 03 ^{ab}
BS1 20 t ha ⁻¹ + F	1.22 ± 0.10 ^b	15.2 ± 0.37 ^a	46.2 ± 2.89 ^a	17.9 ± 1.13 ^a	157 ± 19 ^a	189 ± 77 ^a	9429 ± 893 ^a	435 ± 20 ^b
BS2 10 t ha ⁻¹ + F	1.15 ± 0.12 ^{ab}	14.6 ± 0.18 ^a	43.5 ± 4.21 ^a	17.1 ± 0.99 ^a	156 ± 29 ^a	223 ± 71 ^a	9689 ± 789 ^a	396 ± 17 ^{ab}
BS2 20 t ha ⁻¹ + F	1.16 ± 0.11 ^{ab}	14.4 ± 0.35 ^a	42.9 ± 3.51 ^a	16.6 ± 2.31 ^a	145 ± 34 ^a	177 ± 79 ^a	8398 ± 941 ^a	404 ± 38 ^{ab}

Different letters between the individual treatments stand for a significant difference according to the LSD test ($p < 0.05$).

A significant effect was observed only in treatments with the higher application rates of both BS over a period of 3 years (BS1 20 t ha⁻¹ and BS2 20 t ha⁻¹). In fertilized treatments, the content of total P increased by +6, +18, +3 and +10% in treatments BS1 10 t ha⁻¹ + F, BS1 20 t ha⁻¹ + F, BS2 10 t ha⁻¹ + F and BS2 20 t ha⁻¹ + F, respectively, compared to the fertilized control Co-F. However, a significant effect was found only at the treatment BS1 20 t ha⁻¹ + F. The content of total P in loamy soil increased significantly only in treatments BS2 20 t ha⁻¹ and BS1 20 t ha⁻¹ + F by +53 and +14% compared to their control treatments. A higher content of total P in the soil should also result in a higher content of available P, however, this was only partially confirmed in our study. The content of total P positively correlated with the content of available P ($r = 0.743$, $p < 0.001$) but only in sandy soil. The content of available P in both control treatments on sandy soil was above 200 mg kg⁻¹ which corresponds with a very high content according to criteria for evaluating the

contents of available P in arable soil—Mehlich III. [3,22]. In such cases, fertilization with this nutrient is omitted. In our experiment, the values of available P fluctuated in the range from 336 to 396 mg kg⁻¹ and in the range of 290–362 mg kg⁻¹ in treatments with applied BS without fertilization and with fertilization, respectively (Table 4), but the differences were not significant. No effect on an increase of available P content after application of BS to the soil may be related to the adjustment/enrichment of the resulting biochar/product with phosphorus as was reported by Hossian, et al. [10]. The other reasons might be an uptake of available P by crops, but also the behavior of P in slightly alkaline soil. The accumulation of P in soil depends on the clay content and mineralogical composition, organic matter content, and soil pH [34]. In our study, the content of total P increased in investigated soils, but the content of available P did not significantly change. Biochar substrates contained P, they had an alkaline pH and were additionally applied to slightly alkaline soils. This can be the reason for total P accumulation and a decrease in available P because of chemisorption [35]. Biochar can absorb cations such as Al³⁺, Fe³⁺, and Ca²⁺, which can lead to delayed P absorption or precipitation. Organic molecules could sorb onto biochar reducing its capacity to form chelates [36]. Xu, et al. [35] reported a P sorption increase in acidic soil but a decrease in alkaline soil. The authors attributed an increase in P sorption after biochar addition to Ca-induced P sorption/precipitation. In other studies, the P sorption findings are inconsistent. Soinne, et al. [37] reported that P sorption did not differ in sandy and clay soils after biochar treatments. Conversely, the study of Nelson, et al. [38] indicated a reduction of P leaching after biochar application. Ngatia, et al. [39] reported the biochar properties resulting from biochar production conditions (such as pyrolysis temperature, feedstock, etc.) as the main reason for P sorption and P availability for crops after biochar application. In addition, an increase of pyrolysis temperature (in the biochar production process) results in a loss of O-alkyl carbon and an accumulation of aromatic carbon [40] that favors P sorption [39]. In our case, available P was also affected by soil sorption in different ways depending on the soil type/class, type of BS, or their combination with additional fertilization. In sandy soil and in the BS2 + F treatment, linear dependence was found between CEC and available P. An increase in CEC of 1 mmol kg⁻¹ resulted in an increase in P availability by 4.03 mg kg⁻¹ of soil over a period of 3 years in this treatment (Figure 1A). The SBC also correlated with available P. In sandy soil in treatments BS1 (Figure 1B) and BS2 + F (Figure 1C), the availability of P increased by 2.08 and 3.95 mg kg⁻¹, respectively due to an increase of SBC by 1 mmol kg⁻¹ for the observed period. In loamy soil in treatments BS2 (Figure 1D) and BS1 + F (Figure 1E), the availability of P increased by 3.34 and 3.83 mg kg⁻¹ for each 1 mmol kg⁻¹ of SBC, respectively.

The initial contents of total and available K in both soil types investigated in our study were not significantly different. The application of BS and their combination with additional fertilization increased the content of total K mostly insignificantly even though both substrates contained additional K. In our study in sandy soil, the content of available K moved from good to high stock due to application of BS2 at a rate of 20 t ha⁻¹ and BS1 20 t ha⁻¹ + F. In loamy soil, the content of available K was good in the unfertilized control and satisfactory in the fertilized control. The application of BS with additional fertilization slightly increased available K content, however not significantly. Major, et al. [41] reported that the content of available K increases after incorporation of alkaline biochar into acidic soil. However, in our study, the pH of both soils was slightly alkaline and increased slightly after BS incorporation (Table 3). Of the total content of K in the soil, about 4–5% is available for crops [3]. In our study, significant correlation between total and available K was found only in sandy soil ($r = 0.740$, $p \leq 0.001$). Available K constituted 3.35, 1.96, 1.93, 1.54 and 1.82% of the total K content in treatments Co, BS1 10 t ha⁻¹, BS1 20 t ha⁻¹, BS2 10 t ha⁻¹ and BS2 20 t ha⁻¹, respectively. This observation may suggest that BS eliminated the availability of K of its total content. Biochar can contribute to improving nutrient retention capacity of soil due to its large surface area, porosity, and presence of both non-polar and polar surface sites [42,43]. Biochar reduces nutrient leaching and loss of nutrients through enhancing the ion exchange capacity [11]. When BS were applied in sandy soil together with additional

fertilization, the contents of available K ranged from 1.74 to 2.25% of the total K. In this case, the BS did not have any effect on availability of K of its total content. The same effect was observed in loamy soil, the availability of K ranged from 1.23 to 1.96% of total K. Available K was also affected by soil sorption in different ways depending on the soil type/class, the type of BS or their combination with additional fertilization. In sandy soil, in BS2 treatment, the availability of K increased by 2.54 and 2.52 mg kg⁻¹ soil for each 1 mmol kg⁻¹ SBC (Figure 2A) and CEC (Figure 2B), respectively.

Figure 1. The linear dependence between selected soil properties and P availability for chosen treatments in sandy soil: (A) Cation exchange capacity (CEC) in fertilized treatments; (B) Sum of basic cations (SBC) in nonfertilized treatments; (C) Sum of basic cations (SBC) in fertilized treatments. The linear dependence between sum of basic cations (SBC) and P availability in loamy soil: (D) In chosen nonfertilized treatments; (E) In chosen fertilized treatments. Red circles and * indicate significant correlation at $p \leq 0.05$.

Figure 2. The linear dependence between selected soil properties and K availability for chosen treatments: (A) Sum of basic cations (SBC) in nonfertilized treatments in sandy soil; (B) Cation exchange capacity (CEC) in nonfertilized treatments in sandy soil; (C) Soil pH in fertilized treatments in loamy soil. Red circles and * indicate significant correlation at $p \leq 0.05$.

In loamy soil, a significant negative linear dependence between pH and available K was observed only in the BS1 + F treatment (Figure 2C). In this treatment, increasing soil pH by 1 pH unit could reduce the availability of K by 332 mg kg⁻¹ over a period of 3 years.

Xiao, et al. [44] stated that biochar also contains basic cations, including Ca and Mg. Therefore, it is assumed that after biochar incorporation into the soil, the pH will be neutralized, especially in acidic soils, but also that the content of Ca and Mg cations in the soil will increase. In our study, both tested BS contained total Ca and Mg (BS1: Ca = 42,000 mg kg⁻¹, Mg = 4500 mg kg⁻¹; BS2: Ca = 22,000 mg kg⁻¹, Mg = 5800 mg kg⁻¹). In sandy soils, the total content of Ca and Mg fluctuated in a relatively wide range. The application of BS had no effect on total Ca and Mg content in the soil during the observed period (Table 4). An overall lower content of total Ca and Mg was determined at a higher application rate of both BS compared to the unfertilized control. Such a trend was not found in the case of the application of BS in combination with additional fertilization compared to the fertilized control. The contents of available Ca and Mg changed due to the application of BS compared to the unfertilized control, but due to the large variability of data, no statistical significance was observed. A significant increase in available Ca by +53 and +50% was found in treatments with higher rates of both substrates combined with additional fertilization (BS1 20 t ha⁻¹ + F and BS2 20 t ha⁻¹ + F, respectively) compared to the fertilized control Co-F. Hussain, et al. [40] reported that biochar increases the availability of Ca and Mg in soils, but more pronounced effects shall be observed at lower rather than higher rates, which does not fully correspond to the results of our study (Table 4). In loamy soil, the application of BS did not have effect on content of total and available Ca (Table 4).

In loamy soil, the content of total Mg significantly increased by +11, +32 and +10% in unfertilized treatments BS1 10 t ha⁻¹, BS1 20 t ha⁻¹ and BS2 20 t ha⁻¹, respectively compared to control treatment Co. However, the content of available Mg was not affected. Although the application of BS with additional fertilization did not significantly change the content of total Mg, a significant increase (by +13%) of the content of available Mg was observed in the treatment BS1 10 t ha⁻¹ + F compared to control Co-F. Overall, it should be emphasized that the content of available Mg in all treatments on loamy soil was very high according to the criteria for evaluating available Mg for arable soil [3] and Mg fertilization in such field conditions can be omitted. The application of biochar also enhances nutrient retention by increasing the soil pH [45]. After application of BS, pH in both soils increased or remained slightly alkaline, this affected the availability of Ca and Mg in different ways. In sandy soil, linear relationship was determined between available Ca and soil pH but only in the BS2 treatments (Figure 3A). On the other hand, with increasing SBC and CEC, available Ca content decreased but only in BS2 + F treatments (Figure 3B,C). In sandy soil, the availability of Mg in BS2 increased with the improvement of sorption (i.e., the increase of SBC, CEC and Bs), but no linear relationships were found in other treatments. In loamy soil, higher soil pH decreased Mg availability (Figure 3D) and higher SBC increased Mg availability but only in BS1 + F treatments (Figure 3E). These findings indicate that the relationships between soil pH, sorption and Ca and Mg availability are different and depend on the soil texture, the type of BS and BS combination with additional fertilization.

Figure 3. Cont.

Figure 3. The linear dependence between selected soil properties and Ca availability for chosen treatments in sandy soil: (A) Soil pH in nonfertilized treatments; (B) Sum of basic cations (SBC) in fertilized treatments; (C) Cation exchange capacity (CEC) in fertilized treatments. The linear dependence between selected soil properties and Mg availability for chosen treatments in loamy soil: (D) Soil pH in fertilized treatments; (E) Sum of basic cations (SBC) in fertilized treatments. Red circles and * indicate correlation at $p \leq 0.05$.

4. Conclusions

According to the results of this study, the application of biochar substrates (BS) had a bigger effect on soil pH and sorption parameters in sandy soil when compared to the effect observed in loamy soil. An application dose of 20 t ha^{-1} of both types of BS alone showed the most favorable effects on the sum of basic cations, cation exchange capacity, and base saturation. This study also showed that BS and their combination with additional fertilization increased the total content of P in both soils. At the same time, BS combined with fertilization significantly increased the content of available Ca in sandy soil and available Mg in loamy soil. BS could be utilized at least partially as a suitable substitute to insufficient inputs of some nutrients, especially phosphorus. However, it is extremely important to address P accessibility, especially on alkaline soils, which is a challenge for further research activities in this area. Therefore, in addition to the total supply of nutrients, their availability to plants must be addressed in the future.

Based on the findings of this study, the application of BS demonstrated an improved soil nutrient regime which could assist healthy and sufficient crop production and sustainable soil management in common practice especially in sandy soils and overall, in soils with low fertility in the framework of Central Europe.

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