

Phosphorus and Potassium in Aggregates of Degraded Soils: Changes Caused by Biochar Application

Aymbiré Angeletti da Fonseca,* Danilo Andrade Santos, Celcino Dias Moura-Junior, Renato Ribeiro Passos, and Otacílio José Passos Rangel

The low capacity of degraded soils to provide phosphorus (P) and potassium (K) to plants makes cultivation unviable in these areas. Biochar can increase nutrients availability and improve the physical conditions of soil to maintain their availability over time, including within soil macroaggregates, where P and K are less susceptible to losses. The aim of this study is to understand, how biochar application can change P and K availability in aggregates of degraded soils. The experiment is carried out under controlled conditions following the factorial scheme $2 \times 3 \times 5 \times 2 + 4$, corresponding to two classes of soil, three biochars produced from different raw materials (including stems of elephant grass, EGB, and two types of agricultural wastes: eucalypt stalks, ESB, and sugarcane bagasse, SBB), five rates of biochar, two times and four control treatments. At the end of each time, soil aggregates are divided into two classes by size (macroaggregates and microaggregates) and then P and K availability are measured. The results show that biochar can be a powerful tool to increase P and K availability in soil aggregates. EGB is the most efficient biochar to increase P and K availability, followed by SBB and ESB biochars.

concentrations in degraded areas are usually below plant demand.^[3] Degraded soils are generally acidic, with low nutrient availability, low cation exchange capacity (CEC), and high anion adsorption capacity;^[4] in other words, these areas have low agricultural aptitude and even with periodic fertilization, significant losses of P and K can occur.^[5] Therefore, management practices that can mitigate losses of nutrients are needed to restore degraded areas.

Biochar is a soil conditioner that has been widely studied due to its ability to improve physical, chemical, and biological attributes of soil, and the application of these materials in degraded areas can be a powerful tool to increase P and K availability. Produced by the thermal decomposition of any organic material under a limited supply of oxygen,^[6] biochar has a large specific surface area associated with a high density of surface charges;^[7] moreover, available forms of P and K can be found in its composition.^[8]

Therefore, besides increasing the content of these nutrients, biochar application can improve the physical capacity of soil to keep them available over time.

The main losses of P in degraded areas are caused by the formation of high energy bonds between phosphate anions and mineral colloids of soil, such as iron and aluminum oxides, which restricts the mobility of this nutrient and its absorption by plants.^[9] K, on the other hand, is a monovalent basic cation with high mobility in the soil, thus losses of this nutrient are mainly caused by the leaching process, which can be aggravated in soils with low CEC.^[10] In biochar-modified soils, the surface charges of biochar compete with inorganic colloids of soil for P adsorption, mitigating the intensity of the adsorption process and increasing the P availability.^[11] Furthermore, biochar has a high CEC and can increase the ability of soil to electrostatically retain the available fraction of K.^[8] In addition to improving the capacity of the soil to keep these nutrients available for plants, biochar application can favor the formation of stable macroaggregates in degraded areas,^[12] which affects the potential nutrient supply of the soil.^[13,14] Aggregates are secondary soil particles formed through the interaction between solid constituents of soil.^[14,15] The aggregates <0.25 mm diameter (microaggregates) are compound molecules, formed from organo-mineral associations, that can retain nutrients in their surface charges.^[14,15] These aggregates can join with other microaggregates to form soil

1. Introduction

Land degradation is a progressive process that generates economic and environmental damage that affects the world population and represents a risk for global food security.^[1] The exhaustion of available nutrients in the soil is among the main factors that can aggravate the degradation process, thus, increasing nutrient availability to plants in degraded areas is a key factor for restoration.^[2] Phosphorus (P) and potassium (K) are two of the most limiting nutrients for plant growth and their

A. A. da Fonseca
Soil Department
Universidade Federal de Viçosa
Viçosa, Minas Gerais s/n, Brazil
E-mail: birefonseca@gmail.com; aymbire.fonseca@ufv.br
D. A. Santos, C. D. Moura-Junior, R. R. Passos
Department of Agronomy
Universidade Federal do Espírito Santo
Alegre, Espírito Santo s/n, Brazil
O. J. P. Rangel
Instituto Federal do Espírito Santo, Campus Alegre
Alegre, Espírito Santo 47, Brazil

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/clen.202000366>

DOI: 10.1002/clen.202000366

macroaggregates.^[14,16] Therefore, the stable macroaggregates are larger particles (>0.25 mm) that can provide greater physical protection for nutrients.^[13–16]

The ability of biochars to change all these soil conditions and improve the supply of nutrients, however, is related to the physical-chemical characteristics of these materials, which, under similar pyrolysis conditions, vary mainly according to the raw material used in biochar production.^[7,17] The nutrient content of biochars, for example, is directly related to the inorganic composition of the biomass used, while the functionality and the superficial surface area of these materials are largely related to the concentration of lignin, cellulose, and hemicellulose in the raw material.^[7,8] Among the organic materials that can be used for the production of biochar, the use of agricultural wastes, such as sugarcane (*Saccharum officinarum*) bagasse (SB) and tips of the eucalypt (*Eucalyptus* sp.) stalk (ES), are of great environmental importance.^[18] Moreover, some plants with higher nutrient content that are easily produced, like elephant grass (EG) (*Pennisetum purpureum*), can be a good alternative for the production of nutrient-rich biochar.^[8]

Although the ability of biochars to increase P and K availability in degraded soils is known, there is a lack of knowledge about the dynamics of these nutrients among aggregates of biochar-modified soils. Considering that biochars can: increase the content of P and K in degraded soils, increase the number of loads able to retain these nutrients, and improve soil conditions to form stable macroaggregates; it is likely that, in addition to increasing the availability of P and K in soil microaggregates, the application of biochar favors the availability of these nutrients in macroaggregates, where they are less susceptible to losses. Therefore, the aim of this study was to understand how the application of biochar can change P and K availability in macroaggregates and microaggregates of degraded soils. To do this, five rates of biochar produced from EG stem, SB and tips of ES were applied in two types of degraded soils (Oxisol and Inceptisol). The treatments were evaluated at 42 and 84 days of experiments. The P and K availability was measured in each aggregate class (macroaggregates and microaggregates) to improve knowledge on the dynamic of P and K added to the soil by biochar application.

2. Experimental Section

2.1. Soil Selection and Characterization

Two degraded pastures were selected in Alegre, Espírito Santo State, Brazil. The soil of the first area (20°51'0.18" South, 41°37'0.94" West) was classified as Udepts^[19] (Inceptisol) and the soil of the second area (20°8'32.03" South, 41°35'6.46" West) was classified as Udox^[19] (Oxisol). The collected soil was air-dried and sieved at 2 mm to set up the experiment. Sub-samples of soil were used for their characterization, according to Teixeira (Table 1).^[20]

Sand content was determined by sieving after dispersion with NaOH solution (0.1 mol L⁻¹) and silt and clay were determined by the pipette method.^[21] Soil bulk density was estimated using a graduated cylinder.^[22] Soil moisture at field capacity was measured at 20 kPa using a Richards extractor.^[23] Soil pH was determined using 10 g of soil and 25 mL of water (ratio 1:2.5).^[24] Sodium (Na), K, and P were extracted by Mehlich-1 and measured using flame emission spectrophotometry (K and Na) and col-

Table 1. Physical and chemical characterization of soils.

	Oxisol	Inceptisol
Soil texture ^[43]	Clay	Sand clay loam
Sand (g kg ⁻¹)	317.30	609.60
Silt (g kg ⁻¹)	63.80	122.00
Clay (g kg ⁻¹)	618.90	268.40
Soil bulk density (g cm ⁻³)	1.07	1.33
$\theta^{a)}$ (m ³ m ⁻³)	0.385	0.251
pH (H ₂ O) ^{b)}	4.83	5.35
Phosphorus (mmol kg ⁻¹)	0.17	0.14
Potassium (mmol kg ⁻¹)	0.21	0.63
Sodium (mmol kg ⁻¹)	0.12	0.09
Calcium (cmol _c kg ⁻¹)	0.00	0.44
Magnesium (cmol _c kg ⁻¹)	0.02	0.17
Cation exchange capacity (cmol _c kg ⁻¹)	6.85	3.56
Exchangeable acidity (cmol _c kg ⁻¹)	0.85	0.38
Organic carbon (g kg ⁻¹)	15.60	10.60

^{a)} Soil moisture measured at 20 kPa; ^{b)} Soil/water, 1:2.5, relation.

orimetry (P).^[25,26] Available calcium (Ca) and magnesium (Mg), as well as the exchangeable acidity (EA), were extracted with potassium chloride (1 mol L⁻¹) and determined by an atomic absorption spectrophotometry (Ca and Mg) and titration with NaOH (0.1 mol L⁻¹) (for measuring EA).^[26] The soil organic matter was measured by the oxidation method.^[27]

2.2. Biochar Production and Characterization

Biochar was produced from the stems of EG, SB and tips of ES. Before the carbonization process, the raw materials were passed through a knife mill to homogenize the particle size and placed in crucibles with a capacity of 250 cm³. The crucibles were then sealed to limit the oxygen input into the system during the pyrolysis.

Biochar was produced in a muffle furnace, with a heating ramp of 10 °C min⁻¹ and final temperature of 500 °C. The final temperature was maintained for 20 min and then the biochar was kept in the reactor (turned off) for 12 h, until reaching room temperature. After the carbonization process, the biochar was ground and sieved at 0.210 mm to increase the contact surface with the soil matrix. Sub-samples of EG biochar (EGB), SB biochar (SBB), and ES biochar (ESB) were used for characterization (Table 2).

Carbon, hydrogen, and nitrogen content were determined on a PerkinElmer Series II Analyzer 2400, and the oxygen content was calculated by the difference of the other elements (O = 100 – C – H – N). The O/C and H/C atomic ratios were used to plot the Van-Krevelen diagram (Figure 1).^[28] The pH in water and the electrical conductivity were determined using 0.2 g of biochar and 20 mL of water.^[29,30] The CEC was measured according to Graber et al.^[31] The ash content was determined as the percentage of the initial mass remaining after the sample had been exposed to air at 550 °C for 4 h. The particle density was measured using the balloon method, adapted from Teixeira.^[11] The total content of P and K was obtained by the modified dry-ashing method.^[32] The available fractions of P and K were extracted

Table 2. Biochar characterization.

	Sugarcane bagasse	Elephant grass	Eucalypt stalk
Carbon (%)	59.09	68.53	75.04
Nitrogen (%)	1.06	1.34	0.71
Hydrogen (%)	1.12	1.17	2.34
Oxygen (%)	38.73	28.96	21.91
H/C	0.23	0.20	0.37
O/C	0.49	0.32	0.22
Electrical conductivity ($\mu\text{S cm}^{-1}$)	405.50	6803.33	87.90
Ash (kg kg^{-1})	0.21	0.12	0.01
pH (H_2O) ^{a)}	5.74	7.98	5.09
Cation exchange capacity ($\text{cmol}_c \text{ kg}^{-1}$)	28.5	24.0	10.7
Particle density (g cm^{-3})	1.50	1.69	1.59
Phosphorus _{total} (g kg^{-1})	1.42	5.98	1.22
Potassium _{total} (g kg^{-1})	5.20	36.84	1.12
Phosphorus _{available} (g kg^{-1})	0.39	2.06	0.06
Potassium _{available} (g kg^{-1})	4.83	36.48	0.90
Phosphorus _{water-soluble} (g kg^{-1})	0.18	1.94	0.06
Potassium _{water-soluble} (g kg^{-1})	3.19	27.30	0.86

a) Biochar/water, 0.2:20, relation

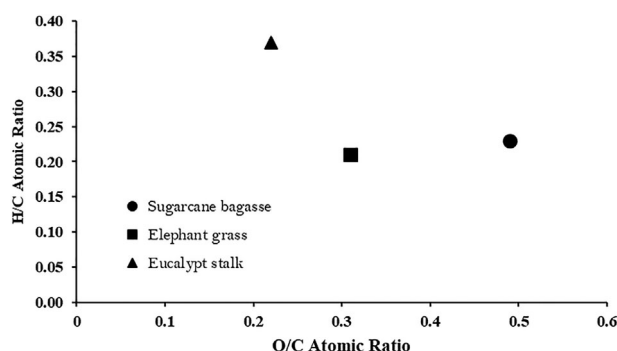


Figure 1. Van-Krevelen diagram of the biochars produced from sugarcane bagasse, stems of elephant grass, and eucalypt stalk.

according to Camps-Arbestain et al.^[33] The water-soluble fractions of P and K were extracted using 1 g of biochar and 20 mL of water. All fractions of P and K in biochars were measured by colorimetry and flame emission spectrophotometry, respectively.

Considering that soil aggregation occurs through the interaction between the solid particles that compose it,^[15] the biochar rates were established according to the volume relationship between soil and biochar (soil/biochar), ensuring similar conditions for the aggregation process in all treatments. The soil/biochar proportions used were 160:1, 80:1, 40:1, 20:1, and 10:1, the equivalent of 0.62%, 1.24%, 2.44%, 4.76%, and 9.09% of biochar.

2.3. Experimental Design and Conduction

The experiment was carried out in a $2 \times 3 \times 5 \times 2 + 4$ factorial scheme, corresponding to two classes of soil (Inceptisol and Oxisol), with three biochars produced from different raw materials

(EGB, SBB, and ESB), five application rates of biochar (0.62%, 1.24%, 2.44%, 4.76%, and 9.09% of biochar), and two times (42 and 84 days after biochar application). Additionally, four control treatments were added to the experiment, including each soil type (Inceptisol and Oxisol) in each incubation time (42 and 84 days). The treatments were installed in a randomized block design, with three repetitions.

Biochar rates were incorporated into 200 cm³ of soil and, afterward, the soil moisture was raised to the field capacity. Room temperature was maintained at 25 °C during the entire experimental period and the soil moisture of each experimental unit was restored every 7 days to stimulate soil aggregation through wetting and drying cycles.

2.4. Soil Aggregate Classes

At the end of the incubation time (42 and 84 days), soil aggregates were divided into two classes by size. Aggregates with a diameter ≥ 0.25 mm were considered as the soil macroaggregate class and aggregates < 0.25 mm were considered the soil microaggregate class. To separate these aggregate classes, an automatic horizontal disturber was used. The proportion of macroaggregates and microaggregates, in each treatment, after the incubation time, are shown in Table S1, Supporting Information.

2.5. Phosphorus and Potassium Availability in Soil Aggregates

The availability of P and K in soil aggregates was evaluated after 42 and 84 days. First, the aggregates were air-dried and sieved at 2 mm, then, a Mehlich-1 solution was used to extract the available form of nutrients. A molecular absorption spectrophotometer and flame spectrophotometer were used to measure the P and K availability, respectively.^[20]

2.6. Statistical Analyses

The effects of biochar application, soil type, incubation time, and raw material type under P and K availability in macroaggregates and microaggregates of soils were evaluated by the following orthogonal contrasts:

- C₁ = Control (without biochar) versus biochar-modified soils
- C₂ = Oxisol versus Inceptisol;
- C₃ = 42 days versus 84 days;
- C₄ = EG versus (SB + ES);
- C₅ = SB versus ES.

Analysis of variance was performed using MS Excel 2010 (Microsoft, USA) to obtain the sum of the residual squares, used to calculate the contrasts significance.^[34]

To assess the effects of increasing the applied rate of biochar produced from EG stems, SB, and tips of ES on P and K availability in macroaggregates and microaggregates of degraded soil, regression analysis was performed using Origin software. The models were selected by the significance of the regression coefficients, obtained by the *t*-test, and by their determination coefficient (*R*²).

Table 3. Orthogonal contrasts used to evaluate phosphorus and potassium availability in aggregates of degraded soils considering the type of soil, raw material used on biochar production, and time (the average values of each treatment are presented in Tables S2 and S3, Supporting Information).

Orthogonal contrast ^{a)}	Phosphorus		Potassium	
	Macroaggregate	Microaggregate	Macroaggregate	Microaggregate
C ₁	76.81*** ^{b)}	148.38***	211.13***	267.63***
C ₂	13.08***	5.06**	−20.20***	45.14***
C ₃	−9.13***	−18.33***	ns	−26.82***
C ₄	−91.24***	−225.22***	−316.37***	−378.24***
C ₅	−3.92*	−4.30**	−9.53***	−15.41***

^{a)} C₁ = control (without biochar) versus biochar-modified soils, C₂: oxisol versus inceptisol, C₃: 42 versus 84 days, C₄: elephant grass stem versus sugarcane bagasse + eucalypt stalk, C₅: sugarcane bagasse versus eucalypt stalk; ^{b)} Values followed by ***, **, * are significant at 0.1%, 1.0%, and 5.0% of probability, respectively.

3. Results

3.1. Potassium Availability

K availability in macroaggregates and microaggregates of biochar-modified soils was higher than in the treatments without biochar (Table 3). The type of soil in which the biochar was

applied also influenced the K availability in macroaggregates and microaggregates (Table 3). When biochar was applied into Oxisol, the K availability in macroaggregates was higher than when these materials were applied into Inceptisol. In contrast, the K availability in microaggregates class was highest in treatments in which Inceptisol soil was used (Table 3).

Available K content in microaggregates decreased with increasing incubation time. However, in soil macroaggregates, the content of available K was not influenced by the increase in incubation time (Table 3).

Among the studied biochar, EGB provided the highest K availability in macroaggregates and microaggregates of degraded soils, followed by biochar produced from SB and ES (Table 3).

Application of high rates of EGB, SBB, and ESB increased the K availability in macroaggregates and microaggregates of degraded soil, regardless of the soil type and incubation time, with a predominance of linear responses (Figures 2 and 3). The exception was in the microaggregates class, in which K availability followed a quadratic response in treatments with the application of EGB (Figures 2 and 3).

3.2. Phosphorus Availability

The P availability in soil aggregates was higher in treatments under the influence of biochar than in treatments without the

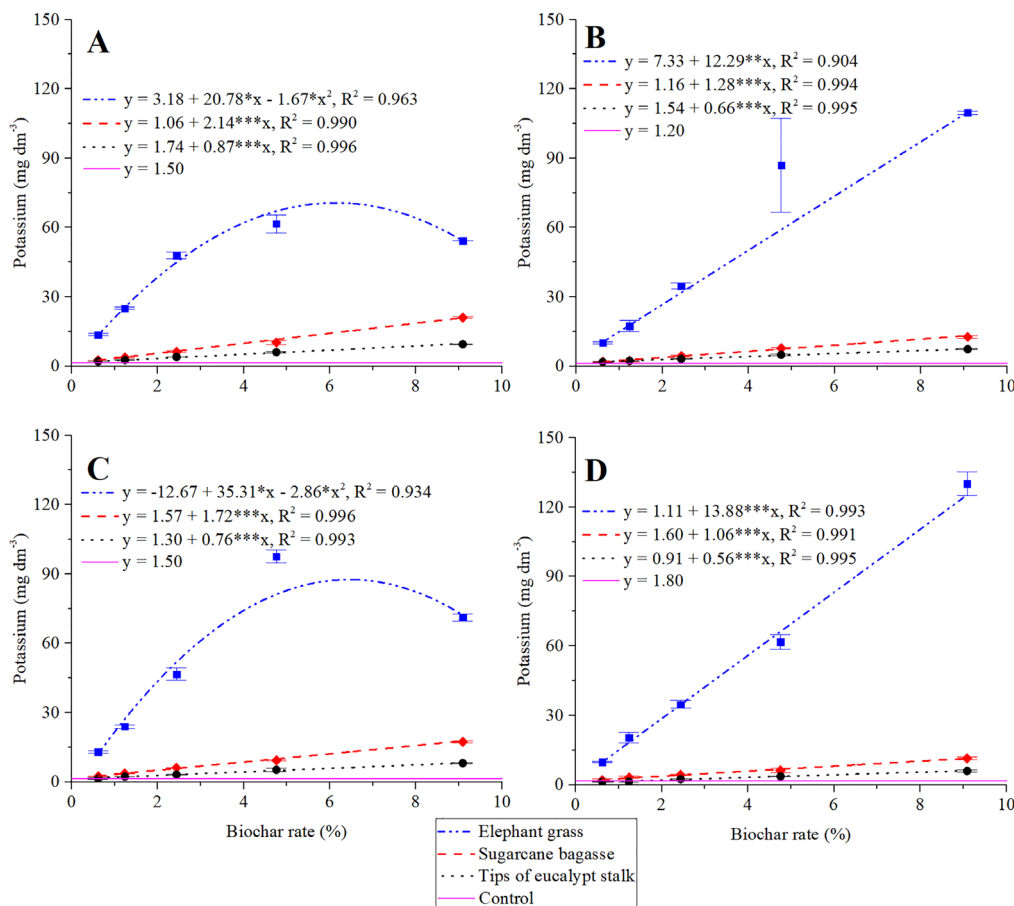


Figure 2. Potassium availability in microaggregates and macroaggregates of Oxisol 42 days ((A) and (B), respectively) and 84 days ((C) and (D), respectively) after biochar application. Regression coefficients followed by ***, ** and * are significant at 0.1%, 1%, and 5%, respectively.

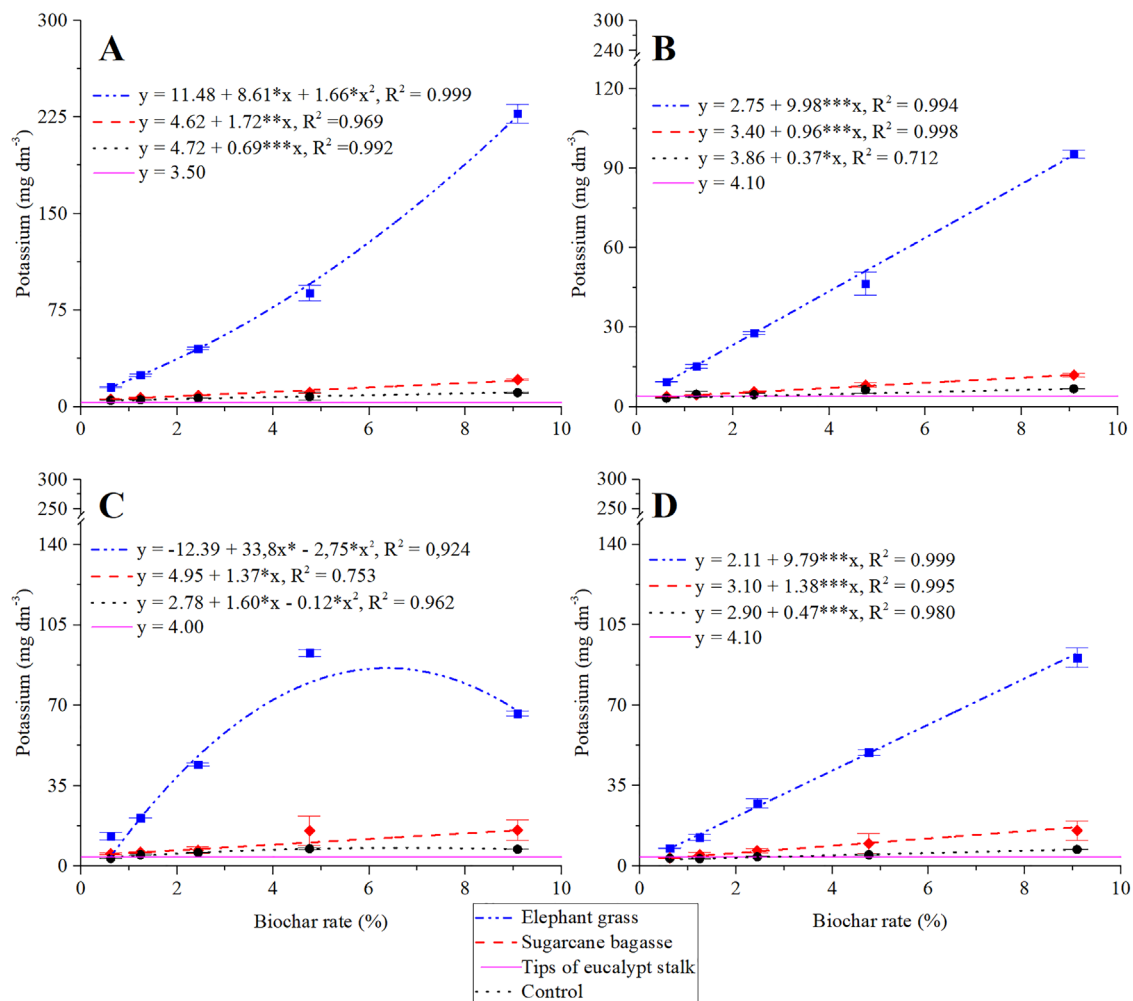


Figure 3. Potassium availability in microaggregates and macroaggregates of Inceptisol 42 days ((A) and (B), respectively) and 84 days ((C) and (D), respectively) after biochar application. Regression coefficients followed by ***, ** and * are significant at 0.1%, 1%, and 5%, respectively.

application of biochar (Table 3). Nevertheless, the P availability was affected by the type of soil wherein biochar was applied (Table 3). When these materials were incorporated into Inceptisol, P availability in macroaggregates and microaggregates was greater than when biochar was incorporated into Oxisol (Table 3).

The incubation time to which the treatments were submitted also influenced the available P content in aggregates of biochar-modified soils. P availability was negatively influenced by the increase of incubation time; therefore, the highest availability of P was observed in treatments submitted to 42 days of incubation (Table 3).

Among the studied biochars, the highest values of available P in soil aggregates occurred in the treatments in which EGB was used (Table 3). Between biochars produced from agricultural wastes, the SBB application provided higher P availability in both macroaggregates and microaggregates compared with the ESB (Table 3).

P availability in macroaggregates and microaggregates of degraded soils was positively affected by increasing rates of EG and SBB (Figures 4 and 5). In the macroaggregates class, the response to the increase of the applied rate of biochar was predominantly

linear. The same comportment was observed in microaggregates when SBB was used. Conversely, with the increase of the EGB rate there was a positive quadratic response in P availability in microaggregates. The increase of the applied rate of ESB generally did not change the availability of P in the aggregates of the studied soils (Figures 4 and 5).

4. Discussion

Biochars are carbonaceous materials formed mainly by C, H, and O, whose constitution includes several cations, such as K.^[7,17] A fraction of the total nutrients present in raw material used for biochar production remains in solid matter after the pyrolysis process and parts of these nutrients are in the available form; therefore, when biochar is incorporated into the soil, there is an increase in K availability.^[35]

As biochar was applied with a grain size of 0.210 mm, the increase of K content occurred first in the microaggregates class (<0.250 mm). A portion of this nutrient can be retained on the surface loads of biochar or even on the loads of the inorganic colloids of soil, and be transported to macroaggregates during the

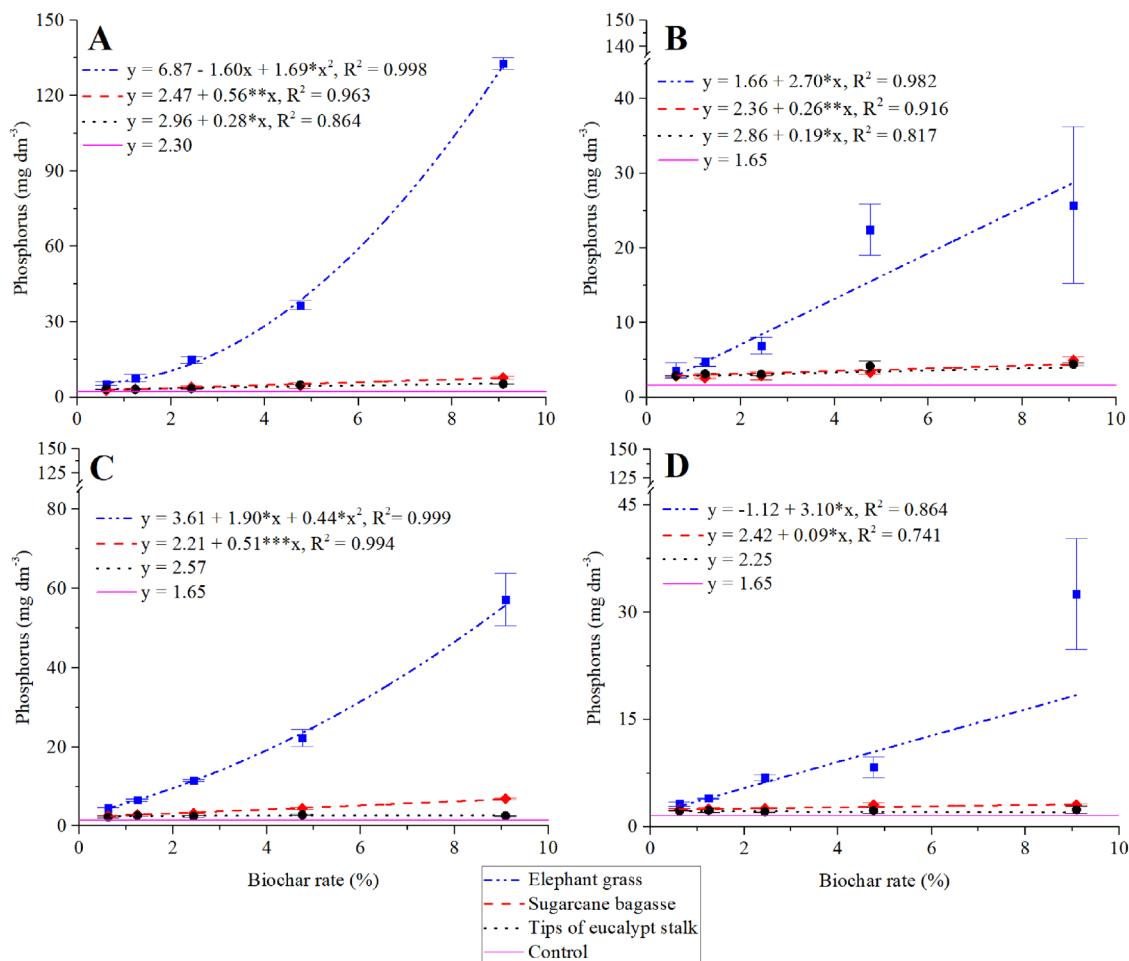


Figure 4. Phosphorus availability in microaggregates and macroaggregates of Oxisol 42 days ((A) and (B), respectively) and 84 days ((C) and (D), respectively) after biochar application. Regression coefficients followed by ***, ** and * are significant at 0.1%, 1%, and 5%, respectively.

aggregation process, thus increasing the availability of K also in this aggregates class.^[36] In biochar-modified soils, the functional groups on the surface of biochar particles can interact with the soil mineral matrix, favoring the formation of stable microaggregates and, later, stable macroaggregates.^[12,14] In addition, these particles of the biochars can retain nutrients like K.^[7,8,11] Therefore, biochar application is advantageous for the formation of aggregates with high K content.

The formation of stable aggregates is a dynamic process in which different forces act to promote the approximation and interaction between solid particles of soil, and the environmental conditions in which the aggregates are formed influence their characteristics.^[15, 37] Macroaggregates formed in soils with high clay content and greater CEC, like Oxisol (Table 1), are more reactive and can retain a greater amount of K ions added by biochar application. On the other hand, Inceptisol has a high sandy content and low CEC, therefore, its macroaggregates had a lower capacity to retain K than the macroaggregates of the Oxisol, so, most of the K added by biochar application remained in the microaggregates class. Regardless of the characteristics of soil, longer incubation time favors the interaction among the organic and inorganic particles of soil, which benefits the aggrega-

tion process.^[14] Thus, it was expected that K ions retained on the surface of these particles would be progressively transported to the soil macroaggregates. However, in this study there was no increase in K availability in macroaggregates after 84 days. Probably because the incubation period was short.

Although K is a macronutrient usually found in biochar composition, its concentrations can vary widely according to the characteristics of the raw material used in its production.^[38] Biochar produced from agricultural wastes (SBB and ESB) had a lower content of K than biochar produced from EG, so, the highest availability of this nutrient occurred in treatments in which EGB was used. The lower availability of K in soil aggregates occurred with the application of ESB. Biochar produced from wood or very lignified materials is generally rich in carbon but has low levels of nutrients,^[39] therefore, the ability of ESB to increase nutrient availability in the soil was lower than the ability of the biochar produced from SB and EG.

Regardless of the raw material used, a fraction of the total K content present in biochar composition is water-soluble (Table 2) and can be quickly released when these materials are incorporated into the soil.^[35] Considering the characteristics of the soils under study, it is unlikely that any K fixation process occurred

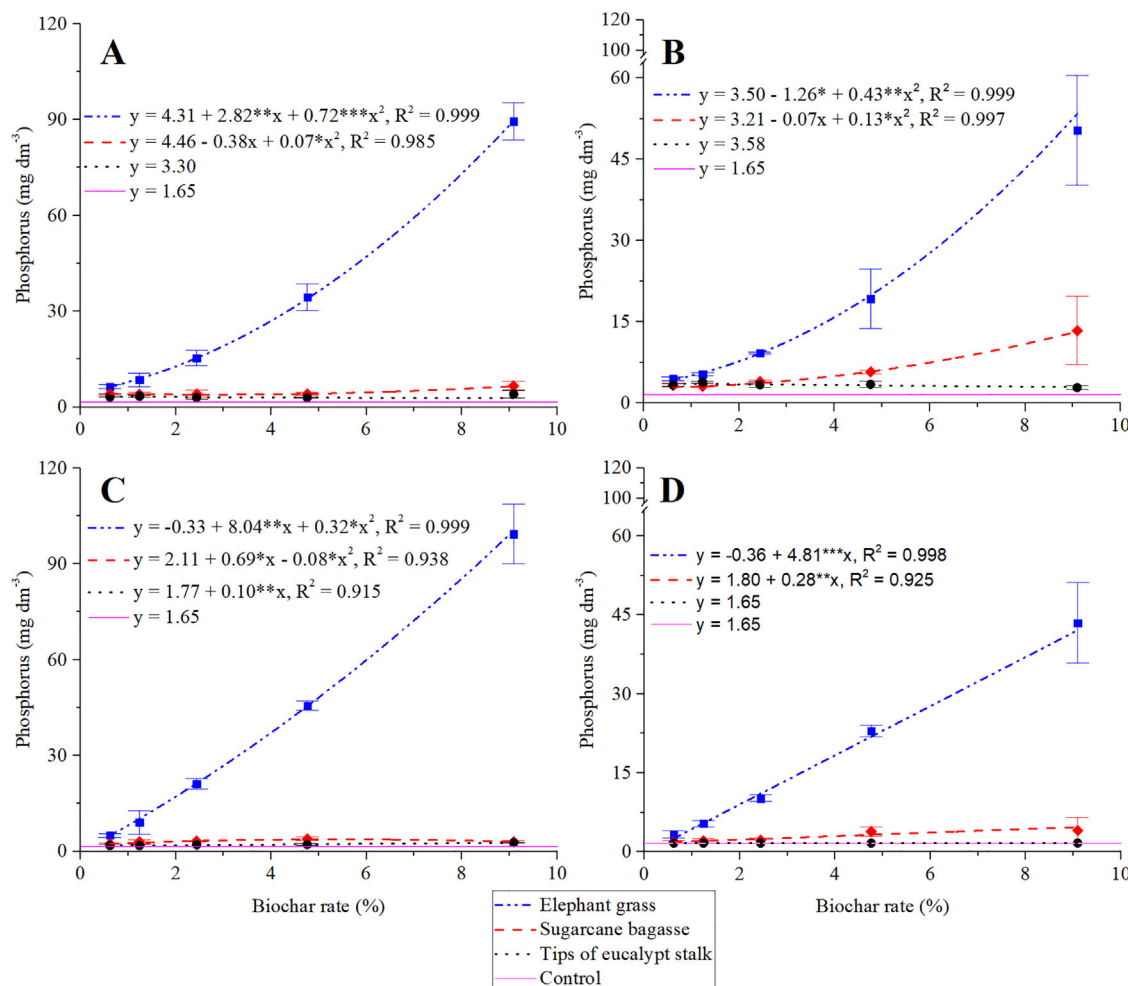


Figure 5. Phosphorus availability in microaggregates and macroaggregates of Inceptisol 42 days ((A) and (B), respectively) and 84 days ((C) and (D), respectively) after biochar application. Regression coefficients followed by ***, ** and * are significant at 0.1%, 1%, and 5%, respectively.

in this experiment, therefore, a linear increase of the K availability in soil aggregates was expected. Nevertheless, in microaggregate class, some treatments showed a quadratic response to the increase rates of EGB. This result indicates that the application of EGB at high rates increased the transfer of K from microaggregates to macroaggregates through the aggregation process,^[14] which makes sense, since increasing the concentration of biochar provides a greater interaction between organic and mineral particles of soil, which benefits the formation of stable aggregates.^[12] When EGB was applied to Oxisol, a soil in which the highest clay contents favor aggregation,^[14,37] this behavior was observed from 42 days of incubation. In treatments where EGB was applied in Inceptisol, on the other hand, this response was only observed at 84 days.

As with K ions, a part of the P present in the raw material remains in the solid matter after its carbonization.^[7,17] A fraction of this nutrient is in available form, so, biochar application can also increase P availability in degraded soils. Nevertheless, P is an anionic ion that is susceptible to several geochemical processes that can reduce its mobility, including complexation, adsorption, and precipitation.^[40] The kinetics of the available P in

soil is marked by a strong interaction between phosphate ions and the soil mineral matrix, which first causes a rapid adsorption of most parts of the added P and over time, a continuous reduction in its availability.^[41] The intensity at which a soil adsorbs P varies according to the quantity and quality of the clay fraction. Highly weathered soils with high clay content, such as Oxisol, have a higher P adsorption capacity than sandy soils,^[8] therefore, the P availability was higher when biochar was applied to Inceptisol. The application of biochar can delay the process of P adsorption but not prevent it from occurring,^[8] so, with the increase in incubation time, there was a decrease in P availability, regardless of the aggregate class.

The P availability in biochar can vary widely according to the characteristics of the raw material used.^[38] The biochar produced from EG had 2.06 g kg⁻¹ of available P, which corresponds to 565 and 3433% of the available P content in the SBB and ESB, respectively. Therefore, the highest P availability occurred in soils where EGB was applied. On the other hand, the lowest P availability was observed in treatments where ESB was used, since wood biochar generally has high aromaticity and low nutrient content.^[39]

A fraction of the total P content in biochar is water-soluble (Table 2) and can be quickly released;^[35] therefore, when higher rates of biochar are applied, more P ions are added into the soil. Nevertheless, as explained above, the P present in soil solution is susceptible to different processes that can limit its availability.^[40] Considering that ESB had only 0.06 g kg⁻¹ of available P in its constitution, when this biochar was used the few P ions added to the treatment were probably adsorbed by the mineral constituents of the soil before the first evaluation (42 days). So, no effect of increasing the applied rate of this biochar was observed in the two evaluated times. Using EGB and SBB, on the other hand, more P ions were added in the soil, thus, it was possible to observe a positive response when increasing the biochar rate. In treatments where a lower intensity of P adsorption was expected (Inceptisol at 42 days), a positive quadratic response was observed in microaggregates and macroaggregates of soils. This result indicates that the positive effects of increasing the rate of biochars on P availability go beyond the simple addition of P ions to the soil. In biochar-modified soils, the surface charges of biochar can compete with the inorganic colloids for P ions, which can reduce the intensity of the adsorption process.^[11] In addition, biochar is generally alkaline material that can increase soil pH, which can also reduce the adsorption of available P in acidic soils.^[42] This same behavior was observed in the microaggregate class whenever biochar EGB was applied.

Biochars produced from agricultural waste (SBB and ESB) have low content of P and K and, thus, less capacity to increase the availability of these nutrients in soil aggregates. Nevertheless the Van-Krevelen diagram indicates that these biochars have lower degree of aromaticity, which may suggest a higher concentration of functional groups.^[28] Although their functionality needs to be confirmed through a more specific technique, such as Fourier transform infrared spectroscopy, the application of mineral fertilizers together with SBB and ESB can likely increase the ability of these biochars to promote the formation of stable and nutrient-rich aggregates.

5. Conclusion

Biochar proved to be a powerful tool to increase P and K availability in soil aggregates, which can be the first step to rebuild soil fertility in degraded areas. This ability of the biochar was mainly related to its nutrients content. The biochar produced from stems of EG had the highest concentration of nutrients and was the most efficient biochar to increase P and K availability in macroaggregates and microaggregates of degraded soils. Although biochars produced from agricultural waste (SBB and ESB) were nutrient-poor, they can also be used to increase the nutrient availability in soil aggregates, which may be partly related to the reactivity of these biochars. Between SBB and ESB, the best results were obtained with the application of the biochar produced from SB. This biochar had more nutrients than ESB and presented less degree of aromaticity than EGB. Considering the importance of reusing agricultural waste, further studies that evaluate the nutrient availability in soil aggregates after the application of biochars together with mineral fertilizers are recommended. These studies should preferably include plants to increase understanding about the dynamics of biochars and their nutrients under field conditions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

D.A.S.: conceptualization, data curation, formal analysis, investigation, methodology, software, supervision, validation, visualization, writing-original draft, writing-review & editing. C.D.M.-J.: data curation, formal analysis, investigation, methodology, resources, software, validation, visualization, writing-review & editing. R.R.P.: conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, supervision, validation, visualization, writing-review & editing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

agricultural wastes, black carbon, fertility rebuild, nutrient availability, sustainable soil management

Received: September 16, 2020

Revised: July 9, 2021

Published online:

- [1] P. C. Peter, *Commun. Soil Sci. Plant Anal.* **2018**, 49, 389.
- [2] T. Li, H. Wang, X. Chen, J. Zhou, *Land Degrad. Dev.* **2017**, 28, 1696.
- [3] R. Pandey, in *Plant Biology and Biotechnology: Plant Diversity, Organization, Function and Improvement* (Eds: B. Bahadur, M. V. Rajam, L. Sahijram, K. V. Krishnamurthy), Springer, New Delhi **2015**, Ch.20.
- [4] B. S. Waswa, P. L. G. Vlek, L. D. Tamene, P. Okoth, D. Mbakaya, S. Zingore, *Geoderma* **2013**, 195–196, 192.
- [5] P. R. Rocha Junior, F. V. Andrade, E. S. Mendonça, G. K. Donagemma, R. B. A. Fernandes, R. Bhattharai, P. K. Kalita, *Sci. Total Environ.* **2017**, 583, 53.
- [6] J. Lehmann, S. Joseph, *Biochar for Environmental Management: Science and Technology*, Earthscan, London **2009**.
- [7] W. Liu, H. Jiang, H. Yu, *Chem. Rev.* **2015**, 115, 12251.
- [8] J. A. Ippolito, K. A. Spokas, J. M. Novak, R. D. Lentz, K. B. Cantrell, in *Biochar for Environmental Management: Science, Technology and Implementation*, 2nd ed. (Eds: J. Lehmann, S. Joseph), Earthscan, London **2015**, Ch.7.
- [9] T. Almeida, E. Pocojeski, C. N. Nesi, J. P. M. Oliveira, L. S. Silva, *Sci. Agrar.* **2016**, 17, 29.
- [10] W. C. Mendes, J. Alves Júnior, P. C. R. Cunha, A. R. Silva, A. W. P. Evangelista, D. Casaroli, *Rev. Bras. Eng. Agric. Ambient.* **2016**, 20, 972.
- [11] M. L. Bornø, D. S. Müller-Stöver, F. Liu, *Sci. Total Environ.* **2018**, 627, 963.
- [12] C. Su, J. Ma, Y. Chen, *Environ. Sci. Pollut. Res.* **2019**, 26, 2662.
- [13] X. Wang, J. Y. Qi, X. Z. Zhang, S. S. Li, A. L. Virk, X. Zhao, X. P. Xiao, H. L. Zhang, *Soil Tillage Res.* **2019**, 194, 104339.

- [14] C. J. Bronick, R. Lal, *Geoderma* **2005**, 124, 3.
- [15] F. Hu, C. Xu, H. Li, S. Li, Z. Yu, Y. Li, X. He, *Soil Tillage Res.* **2015**, 147, 1.
- [16] J. M. Tisdall, J. M. Oades, *J. Soil Sci.* **1982**, 33, 141.
- [17] K. Weber, P. Quicker, *Fuel* **2018**, 217, 240.
- [18] R. R. Passos, R. W. Silva, C. F. Barbosa, E. S. Mendonça, O. J. P. Rangel, in *Tópicos Especiais em Produção Vegetal*, Vol. 5 (Eds: A. Ferreira, J. C. Lopes, M. F. S. Ferreira, T. C. V. Soares), CAUFES, Alegre **2016**, Ch.25.
- [19] Soil Survey Staff, Keys to soil taxonomy (12th ed.), United States Department of Agriculture, Washington, DC **2014**.
- [20] P. C. Teixeira, D. K. Donagemma, A. Fontana, W. G. Teixeira, *Manual de Métodos de Análise de Solo*, Embrapa, Rio de Janeiro **2017**.
- [21] B. G. Almeida, G. K. Donagemma, H. R. Ruiz, J. A. Braidia, J. H. M. Viana, J. M. M. Reichert, L. B. Oliveira, M. B. Ceddia, P. S. Wadt, R. B. A. Fernandez, R. R. Passos, S. C. F. Dechen, V. A. Klein, W. G. Teixeira, *Comunicado Técnico 66 – Padronização de Métodos Para Análise Granulométrica no Brasil*, Embrapa, Rio de Janeiro **2017**.
- [22] B. G. Almeida, J. H. M. Viana, W. G. Teixeira, G. K. Donagemma, in *Manual de Métodos de Análise de Solo*, Vol. 1 (Eds: P. C. Teixeira, G. K. Donagemma, A. Fontana, W. G. Teixeira), Embrapa, Rio de Janeiro **2017**, Ch. 7.
- [23] W. G. Teixeira, S. B. Behring, in *Manual de Métodos de Análise de Solo*, Vol. 1 (Eds: P. C. Teixeira, G. K. Donagemma, A. Fontana, W. G. Teixeira), Embrapa, Rio de Janeiro **2017**, p. 4.
- [24] P. C. Teixeira, D. V. B. Campos, M. F. C. Saldanha, in *Manual de Métodos de Análise de Solo*, Vol. 2 (Eds: P. C. Teixeira, G. K. Donagemma, A. Fontana, W. G. Teixeira), Embrapa, Rio de Janeiro **2017**, Ch. 1.
- [25] P. C. Teixeira, D. V. B. Campos, M. F. C. Saldanha, in *Manual de Métodos de Análise de Solo*, Vol. 2 (Eds: P. C. Teixeira, G. K. Donagemma, A. Fontana, W. G. Teixeira), Embrapa, Rio de Janeiro **2017**, Ch. 2.
- [26] P. C. Teixeira, D. V. B. Campos, S. R. Bianchi, D. V. Pérez, M. F. C. Saldanha, in *Manual de Métodos de Análise de Solo*, Vol. 2 (Eds: P. C. Teixeira, G. K. Donagemma, A. Fontana, W. G. Teixeira), Embrapa, Rio de Janeiro **2017**, p. 3.
- [27] A. Fontana, D. V. B. Campos, in *Manual de Métodos de Análise de Solo*, Vol. 3 (Eds: P. C. Teixeira, G. K. Donagemma, A. Fontana, W. G. Teixeira), Embrapa, Rio de Janeiro, **2017**, Ch. 1.
- [28] A. Rivas-Ubach, Y. Liu, T. S. Bianchi, N. Toli, C. Jansson, L. Paša-Toli, *Anal. Chem.* **2018**, 90, 6152.
- [29] S. Rajkovich, A. Enders, K. Hanley, C. Hyland, A. R. Zimmerman, J. Lehmann, *Biol. Fertil. Soils* **2012**, 48, 271.
- [30] B. Singh, M. M. Dolk, Q. Shen, M. Camps-Arbestain, in *Biochar: A Guide to Analytical Methods* (Eds: B. Singh, M. Camps-Arbestain, J. Lehmann), CRC Press, London **2017**, p. 3.
- [31] E. R. Graber, B. Singh, K. Hanley, J. Lehmann, in *Biochar: A Guide to Analytical Methods* (Eds: B. Singh, M. Camps-Arbestain, J. Lehmann), CRC Press, London **2017**, Ch. 7.
- [32] A. Enders, J. Lehmann, *Commun. Soil Sci. Plant Anal.* **2012**, 43, 1042.
- [33] M. Camps-Arbestain, Q. Shen, W. Tao, L. V. Zwieten, J. Novak, in *Biochar: A Guide to Analytical Methods* (Eds: B. Singh, M. Camps-Arbestain, J. Lehmann), CRC Press, London **2017**, p. 10.
- [34] V. V. H. Alvarez, in *Reflexões sobre a Produção Científica* (Ed: V. V. H. Alvarez), Brazilian Society of Soil Science, Viçosa **2020**, Ch.11.
- [35] H. Yuan, T. Lu, Y. Wang, Y. Chen, T. Lei, *Geoderma* **2016**, 267, 17.
- [36] H. Rens, T. Bera, A. K. Alva, *Water, Air, Soil Pollut.* **2018**, 229, 281.
- [37] S. Dultz, S. K. Woche, R. Mikutta, M. Schrapel, G. Guggenberger, *Appl. Clay Sci.* **2019**, 170, 29.
- [38] N. Prakongkep, R. J. Gilkes, W. Wiriyaakitnateekul, *J. Plant Nutr. Soil Sci.* **2015**, 178, 732.
- [39] N. A. Qambrani, M. M. Rahman, S. Won, S. Shim, C. Ra, *Renewable Sustainable Energy Rev.* **2017**, 79, 255.
- [40] R. Chintala, T. E. Schumacher, L. M. McDonald, D. E. Clay, D. D. Malo, S. K. Papiernik, S. A. Clay, J. L. Julson, *Clean: Soil, Air, Water* **2014**, 42, 626.
- [41] R. S. Guedes, L. C. A. Melo, L. Vergütz, A. Rodríguez-Vila, E. F. Covelo, A. R. Fernandes, *Soil Tillage Res.* **2016**, 162, 46.
- [42] R. B. Fidel, D. A. Laird, M. L. Thompson, M. Lawrinenko, *Chemosphere* **2017**, 167, 367.
- [43] Soil Science Division Staff, in *Soil Survey Manual*, United States Department of Agriculture, Washington, DC **2017**, Ch. 3.