



# Amending a tropical Arenosol: increasing shares of biochar and clay improve the nutrient sorption capacity

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## Abstract

Tropical Arenosols may be challenging for agricultural use, particularly in semi-arid regions. The aim of this study was to evaluate the impact of the addition of increasing shares of biochar and clay on the nutrient sorption capacity of a tropical Arenosol. In batch equilibrium experiments, the sorption of ammonium-N ( $\text{NH}_4^+\text{-N}$ ), nitrate-N ( $\text{NO}_3^-\text{-N}$ ), potassium ( $\text{K}^+$ ), and phosphate-P ( $\text{PO}_4^{3-}\text{-P}$ ) was quantified for mixtures of an Arenosol with increasing shares of biochar and clay (1%, 2.5%, 5%, 10%, 100%) and the unmixed Arenosol, biochar, and clay. The mid-temperature biochar was produced from *Prosopis juliflora* feedstock; the clayey material was taken from the sedimentary parent material of a temporarily dry lake. Only the Arenosol–biochar mixture with 10% biochar addition and the biochar increased the  $\text{NH}_4^+\text{-N}$  maximum sorption capacity ( $q_{\max}$ ) of the Arenosol, by 34% and 130%, respectively. The  $q_{\max}$  of  $\text{PO}_4^{3-}\text{-P}$  slightly increased with ascending biochar shares (1–10%) by 14%, 30%, 26%, and 42%, whereas the undiluted biochar released  $\text{PO}_4^{3-}\text{-P}$ . Biochar addition slightly reduced  $\text{NO}_3^-\text{-N}$  release from the Arenosol but strongly induced  $\text{K}^+$  release. On the other hand, clay addition of 10% and clay itself augmented  $q_{\max}$  of  $\text{NH}_4^+\text{-N}$  by 30% and 162%; ascending clay rates (1–100%) increased  $q_{\max}$  for  $\text{PO}_4^{3-}\text{-P}$  by 78%, 130%, 180%, 268%, and 712%. Clay rates above 5% improved  $\text{K}^+$  sorption; however, no  $q_{\max}$  values could be derived. Sorption of  $\text{NO}_3^-\text{-N}$  remained unaffected by clay amendment. Overall, clay addition proved to enhance the nutrient sorption capacity of the Arenosol more effectively than biochar; nonetheless, both materials may be promising amendments to meliorate sandy soils for agricultural use in the semi-arid tropics.

## Highlights

- Biochar addition slightly increased  $\text{NH}_4^+\text{-N}$  and  $\text{PO}_4^{3-}\text{-P}$  sorption, reduced  $\text{NO}_3^-\text{-N}$  release but triggered  $\text{K}^+$  release.
- Clay addition enhanced sorption of  $\text{NH}_4^+\text{-N}$ ,  $\text{K}^+$ , and  $\text{PO}_4^{3-}\text{-P}$  better than biochar but had no effect on  $\text{NO}_3^-\text{-N}$ .
- Both substrates can contribute to fertility of Arenosols by increasing their nutrient content and sorption capacity.

**Keywords** Coarse-textured soils · Biochar · Clay · Batch equilibrium experiment · Sorption isotherms

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## 1 Introduction

Arenosols are among the most abundant soil types worldwide. They cover an area of about 1300 million ha, corresponding to roughly 10% of the land surface. Even though Arenosols can be found globally, they predominate in vast areas of arid and semi-arid regions (IUSS Working Group WRB 2014; Yost et al. 2019). This also includes the Itaparica region, located in the state of Pernambuco in the north-east of Brazil (Araújo Filho et al. 2013). These coarse-textured soils have low contents of organic carbon (C) and clay, resulting in limited capacity to retain water and nutrients (Huang and Hartemink 2020). One possible land management strategy to meliorate soil fertility could be the application of soil amendments such as biochar and clay. By increasing soil C and clay content, the nutrient retention of the Arenosol may be enhanced, leading to more efficient fertiliser use and hence contributing to food security in the region.

Many studies in recent years have revealed the positive effects of biochar amendment on physical and chemical soil properties (Beusch 2021), such as the increase of cation exchange capacity (CEC) (Das et al. 2021; Liang et al. 2006) and soil water-holding capacity (e.g., Abel et al. 2013; Bruun et al. 2014; Hien et al. 2021). Furthermore, an increase in crop yield has been documented for different biochars, soil types, and regions (e.g., Gopal et al. 2020; Jeffery et al. 2011; Steiner et al. 2007; Xu et al. 2015; Zhang et al. 2015). Various studies have proved the potential of biochars to retain nutrients in the soil. Most of them focused on the inorganic forms of nitrogen (N); ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) sorption were, for instance, reported by Aghoghovwia et al. (2020), Fatima et al. (2021), Kameyama et al. (2012), and Pratiwi et al. (2016). Moreover, pyrolysis conditions determine the potential of the biochar to retain  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . However, sorption of  $\text{NH}_4^+$  decreases with increasing production temperatures of biochar (Gai et al. 2014; Li et al. 2018; Takaya et al. 2016), whereas  $\text{NO}_3^-$  sorption increases with higher temperatures (Fatima et al. 2021; Yao et al. 2012; Zheng et al. 2013). The literature, however, is not consistent since other studies report no sorption for  $\text{NH}_4^+$  (Alling et al. 2014) and no sorption or even release of  $\text{NO}_3^-$  with the addition of biochar to soils (Hale et al. 2013; Hollister et al. 2013; Gai et al. 2014; Li et al. 2018). In contrast to nitrogen, only a few experiments addressed sorption or retention of potassium (K) by biochars. Most of them did not report any sorption but strong K release from biochars (Limwikran et al. 2018; Raave et al. 2014; Rens et al. 2018; Widowati et al. 2014). For phosphate ( $\text{PO}_4^{3-}$ ), several studies revealed sorption to biochar (Rashmi et al. 2020; Takaya et al. 2016; Wang et al. 2021), but different factors were assumed to be responsible for  $\text{PO}_4^{3-}$  sorption. For

example, biochar feedstock (Gronwald et al. 2015), soil acidity (Ghodsad et al. 2022), or higher process temperature (Trazzi et al. 2016; Zhang et al. 2016) were hypothesised as main factors controlling sorption, while Fatima et al. (2021) and Morales et al. (2013) reported more  $\text{PO}_4^{3-}$  sorption by biochars produced with lower temperatures. However, Alling et al. (2014) and Schneider and Haderlein (2016) found only weak  $\text{PO}_4^{3-}$  sorption, while other studies reported none at all (Morales et al. 2021; Yao et al. 2012; Zheng et al. 2013). Overall, the knowledge about nutrient sorption to biochar remains insufficient. Furthermore, the majority of sorption studies were conducted with pure biochar; only a small number of experiments addressed different biochar-soil ratios.

Another possibility to meliorate sandy soils is to add clayey material to increase water and nutrient retention capacities. However, compared to the number of biochar-related studies, this practice was only considered by a few studies. The majority of research regarding clay addition has been conducted on sandy soils, mostly in semi-arid and arid climates. Addition of clay to soils is reported to enhance their water-use efficacy (Al-Omran et al. 2005; Suzuki et al. 2007), increase the soil water content (Mi et al. 2021), reduce the hydrophobicity of sandy soils (Blackwell 2000; Cann 2000; McKissock et al. 2002; Shanmugam and Abbott 2015), foster the formation of organo-mineral complexes (Reuter 2001), reduce soil erosion and restrain land degradation (Pi et al. 2021), and increase CEC and soil organic matter content (Hall et al. 2010; Karbout et al. 2021; Schapel et al. 2018). Clay amendment also led to improved plant nutrition, in particular for K, and enhanced water infiltration and water distribution (Hall et al. 2010). In a study about *terra preta* practice in a tropical rain forest, Schritt et al. (2020) outlined the potential of biochar and clay addition to soils and composts to close nutrient cycles. All these meliorations of soil properties may have contributed to the increase of yield and the improvement of yield quality after clay addition that was reported in several studies (e.g., Al-Omran et al. 2005; Hall et al. 2010; Mi et al. 2020; Reuter 2001). Other studies focused on adsorption of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , or  $\text{PO}_4^{3-}$  from aqueous solutions to clayey material to investigate sediment–water interactions and to test their suitability for the construction of wetlands or for removal of ammonium from waste water (Alshameri et al. 2018; Baker and Fraij 2010; Durn et al. 2016; Lazaratou et al. 2020; Zhu et al. 2011). However, even though clayey material is not considered as a soil amendment, these studies contribute to a better understanding of the sorption mechanisms of nutrients to clay. In contrast, only some studies have addressed the effects of clay amendment on nutrient dynamics in soils. Reuter (1994) reported a decrease in leaching of phosphorus (P) and K after clay addition, Dempster et al. (2012) described a decrease in  $\text{NH}_4^+$  leaching, but no effect for

NO<sub>3</sub><sup>-</sup>, Nguyen and Marschner (2013) found a reduction of N and P leaching, and Ye et al. (2019) reported a reduction of NO<sub>3</sub><sup>-</sup> leaching. In a field experiment, Beusch et al. (2019) observed a significant reduction of NH<sub>4</sub><sup>+</sup>-N and K<sup>+</sup> leaching for clay-amended sandy soils, which remained relatively stable for 1.5 years, but a contrasting increase of NO<sub>3</sub><sup>-</sup>-N leaching. Tahir and Marschner (2017) found an increase of NH<sub>4</sub><sup>+</sup>-N and P sorption of an Arenosol after the addition of a high-smectite soil collected from a Vertisol. However, the knowledge about the effects of clay amendments on the sorption and retention of nutrients remains limited.

The objective of this study was to enhance the nutrient sorption capacity of an Arenosol from north-eastern Brazil by using locally available and inexpensive materials. Locally produced biochar made of *Prosopis juliflora* (Sw.) DC. and clayey material, collected from the A-horizon of a Vertisol that developed at the bottom of a temporarily dry lake, were mixed with the Arenosol in different ratios. To illuminate the sorption behaviour of different nutrients, sorption isotherms according to Langmuir and Freundlich were derived for NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N, K<sup>+</sup>, and PO<sub>4</sub><sup>3-</sup>-P for different mixtures of the Arenosol with biochar and clay, respectively. We hypothesised that the addition of biochar and clay would have significant effect on the sorption of (i) NH<sub>4</sub><sup>+</sup>-N, (ii) NO<sub>3</sub><sup>-</sup>-N, (iii) K<sup>+</sup>, and (iv) PO<sub>4</sub><sup>3-</sup>-P. In particular, we expected that biochar would increase the sorption of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N, and that clay would increase the sorption of NH<sub>4</sub><sup>+</sup>-N, K<sup>+</sup>, and PO<sub>4</sub><sup>3-</sup>-P compared to unamended Arenosol.

## 2 Material and methods

### 2.1 Characterisation of substrates

All materials used in this study have their origin at the site of a field experiment (8° 57' 24.1" S and 38° 15' 00.4" W), located in the Itaparica area, Pernambuco state, north-eastern Brazil. Details about the field site can be found in Beusch et al. (2019) and Mertens et al. (2017a, b). For the batch experiment in this study, material from the same site was used. The soil studied is a Protic Arenosol (according to IUSS Working Group WRB 2014). It has a sandy texture with low contents of silt and clay and a low pH (Table 1). For this experiment, a mixed soil sample was taken from 0 to 30 cm depth, air-dried, and sieved to 2 mm.

The biochar was made from trunks and branches of the Fabaceae tree *Prosopis juliflora* (Sw.) DC., which is an invasive species in the area (Sena et al. 2021) and has, other than endemic Caatinga species, no restrictions in cutting. It was produced through slow pyrolysis by a local charcoal burner in a traditional way, using a clay kiln with a burrow sealed with corrugated sheet. No data on pyrolysis temperature and residence time are available. However,

**Table 1** Standard chemical and physical substrate properties for chemical parameters  $n = 3$ , for physical parameters (specific surface area (SSA), grain size distribution)  $n = 2$ ; SSA was determined in N<sub>2</sub> (\*) or CO<sub>2</sub> (†); n.d. not determined

Properties	Unit	Arenosol 0B/0C	Biochar 100B	Clay 100C
pH (H <sub>2</sub> O)		5.1	9.1	8.3
pH (KCl)		4.2	8.2	7.3
Total C	g kg <sup>-1</sup>	1.78	852.71	17.07
Total N	g kg <sup>-1</sup>	0.21	4.76	0.67
Total Al	g kg <sup>-1</sup>	4.91	0.24	64.14
Total Fe	g kg <sup>-1</sup>	2.10	0.20	61.00
Total Mn	g kg <sup>-1</sup>	0.00	0.01	0.87
Total Ca	g kg <sup>-1</sup>	n.d.	6.50	38.00
Total Mg	g kg <sup>-1</sup>	0.12	1.17	28.77
Total Na	g kg <sup>-1</sup>	n.d.	1.14	0.23
Total K	mg kg <sup>-1</sup>	n.d.	7697.75	17533.69
Total P	mg kg <sup>-1</sup>	42.93	580.79	488.31
Plant-available K	mg kg <sup>-1</sup>	27.45	1060.40	288.67
Plant-available P	mg kg <sup>-1</sup>	1.24	71.20	9.80
Cation exchange capacity	cmol <sub>c</sub> kg <sup>-1</sup>	0.87	n.d.	72.57
SSA	m <sup>2</sup> g <sup>-1</sup>	1.80*	249.15 <sup>†</sup>	108.25*
Clay	%	4.3	n.d.	69.8
Silt	%	0.4	n.d.	30.2
Sand	%	95.3	n.d.	0.0

For analytical methods, see Sect. 2.2

**Table 2** Biochar specific properties ( $n = 3$ )

Properties	Unit	Biochar 100B
Total H	g kg <sup>-1</sup>	31.6
Total O	g kg <sup>-1</sup>	120.7
Total S	g kg <sup>-1</sup>	1.0
Molar H:C		0.46
Molar O:C		0.11
Ash content	%	2.2
Volatile matter	%	19.1
Estimated pyrolysis temperature	°C	Approx. 450

Molar H:C and O:C ratios and O content were calculated; pyrolysis temperature was estimated based on biochar properties. For details, see Sect. 2.1

an estimation of the production temperature based on temperature-controlled parameters like hydrogen (H), oxygen (O), C, ash, and volatile matter (VM) content, along with molar O:C and H:Cratios (e.g., Chen et al. 2008; Spokas 2010; Zhao et al. 2013) was possible. Our data

(Table 2) correspond well to those given by Trompowsky et al. (2005) for two woody biochars made of *Eucalyptus saligna* and *Eucalyptus grandis* and to a pine biochar by Ronsse et al. (2012). These biochars were produced under slow pyrolysis conditions at a temperature of 450 °C. Consequently, we assume an approximate pyrolysis temperature of 450 °C, indicating a medium-temperature biochar, according to Chen et al. (2015). Before use, the air-dried biochar was pestled and sieved to < 0.5 mm. We refrained from washing the biochar before the conduction of the experiment to simulate real-life field practice in tropical agriculture, where washing of large amounts of biochar would (i) not be economically feasible and (ii) lead to a loss of desirable nutrients.

The clayey material applied in this experiment is an A-horizon of a Vertisol, originating from the sediment of a periodically dried-up lake close to the experimental site described in Beusch et al. (2019) and dominated by a smectitic mineralogy. It has a high clay content of almost 70%, leading to a large specific surface area (SSA) and large CEC (Table 1). The clay contains the following clay minerals: 40% to 60% smectite, 10% to 30% illite, and 20% to 30% kaolinite, plus less than 10% calcium carbonate, organic material, and iron oxides (Mertens et al. 2017a). For this experiment, mixed samples were taken from 0 to 30 cm depth, air-dried, carefully crushed and sieved to < 0.5 mm.

## 2.2 Laboratory analyses

Before all analyses, substrates were air-dried and sieved: Arenosol to < 2 mm, clay and biochar to < 0.5 mm. Substrates were ground in tungsten carbide vessels (MM200, Retsch, Haan, Germany) for analysis of C, H, N, and sulfur (S). The pH was analysed in millipore water and in 1 M KCl, in a soil/solution ratio (w/v) of 1:2.5 using an inoLab pH/Cond Level 1, SenTix 41 electrode (WTW, Weilheim, Germany). Electric conductivity (EC) was analysed with the same device, using a WTW TetraCon 325 conductivity cell. Soil texture was determined by sieving and sedimentation according to DIN ISO 11277. Total C, H, N, and S concentrations were analysed in triplicate after dry combustion, using an Elementar Analyzer (Vario EL III, Elementar, Hanau, Germany), while H was only derived for biochar. Effective CEC was analysed for clay and the Arenosol using 1 M  $\text{NH}_4\text{Cl}$  extraction with a soil/solution ratio (w/v) of 1:20. The concentrations of extracted aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), sodium (Na), and K were analysed with an ICP-OES iCAP 6000 ICP Spectrometer (Thermo Fisher Scientific, Dreieich, Germany). Plant-available P and K were determined after extraction with 0.05 M calcium-acetate-lactate in a soil/solution ratio (w/v) of 1:20. Analysis was conducted with the ICP-OES (iCAP 6000 ICP Spectrometer, Thermo Fisher

Scientific, Dreieich, Germany). SSA for biochar, Arenosol, and clay was measured by gas adsorption, applying the Brunauer–Emmett–Teller (BET) equation (ISO 9277:1995) in an Autosorb-1 (Quantachrome, Odelzhausen, Germany), using  $\text{N}_2$  as an adsorbate for clay and Arenosol, and carbon dioxide ( $\text{CO}_2$ ) for biochar. For further methodological details of the conducted gas adsorption measurements, see Wagner and Kaupenjohann (2014). Total contents of Al, Fe, Mn, Ca, Mg, Na, K, and P were determined after digestion with  $\text{HNO}_3$  (biochar) and *aqua regia* (Arenosol and clay), respectively. All substrates were ground and dried at 105 °C prior to digestion. For  $\text{HNO}_3$  digestion, 5 mL of 69%  $\text{HNO}_3$  (suprapur) was added to 250 mg biochar; for *aqua regia* digestion, 10 mL *aqua regia* (1 part 69%  $\text{HNO}_3$  suprapur, three parts 37% HCl suprapur) was added to 500 mg Arenosol and clay, respectively. All extracts were heated in pressure-tight vessels for 6 h at 185 °C and were analysed with ICP-OES. An overview of the chemical and physical parameters of the materials is given in Table 1. Some parameters were derived for biochar only: Volatile matter content was determined in triplicate according to DIN 51720 in crucibles covered with lids to avoid oxygen contact for 7 min under 900 °C in muffle furnace LV 5/11, controller P330, controller S27” (Nabertherm, Lilienthal, Germany); ash content was determined in triplicate according to DIN 51719 for 60 min under 815 °C in the same furnace; oxygen content was calculated according to DIN 51733 by subtracting ash content, C, H, N, and S (% w/w each) from 100; and molar H:C and O:C ratios were calculated for the biochar used (Table 2).

The aqueous solutions obtained from the batch experiments were stored at  $-18$  °C until analysis. Directly after melting the aqueous solutions,  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  were analysed by CFA Auto Analyzer 3 MT7 (SEAL Analytical, Norderstedt, Germany). In the concentration range from 0 to 5  $\text{mg L}^{-1}$ ,  $\text{PO}_4^{3-}\text{-P}$  was measured with the same CFA Auto Analyzer, when above 5  $\text{mg L}^{-1}$ , P was detected by ICP-OES iCAP 6000 ICP Spectrometer (Thermo Fisher Scientific, Dreieich, Germany). In the range from 0 to 2  $\text{mg L}^{-1}$ ,  $\text{K}^+$  was analysed by flame AAS (1100B Perkin Elmer, Rodgau, Germany) and caesium was added to avoid ionisation;  $\text{K}^+$  concentrations above 2  $\text{mg L}^{-1}$  were analysed by ICP-OES iCAP 6000 ICP Spectrometer (Thermo Fisher Scientific, Dreieich, Germany).

## 2.3 Batch experiment

Several mixtures of Arenosol–biochar and Arenosol–clay, as well as the plain Arenosol, biochar, and clay were tested for their sorption capacity for  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{K}^+$ , and  $\text{PO}_4^{3-}\text{-P}$  according to OECD guideline 106 for testing of chemicals (Adsorption/Desorption using a Batch Equilibrium Method OECD 2000). Where necessary, the method was adjusted to the experimental needs of this study.

Labelling of the samples is based on the percentage of soil conditioner mixed with the Arenosol, “B” refers to biochar, “C” to clay. The label 0B/0C corresponds to the unamended Arenosol, with no biochar or clay addition; 1B refers to a biochar content of 1% (w/w), whereas 100C refers to the clay itself, 100B to the biochar itself, etc. All sorption experiments have been conducted with unamended Arenosol (0B/0C), biochar (100B), clay (100C), and different mixtures of the Arenosol with biochar and clay, respectively. The mixtures cover a realistic range of applicable biochar and clay amounts (1%, 2.5%, 5%, 10%; w/w).

The nutrient solution was composed to reflect a realistic fertilisation scheme. Batch experiments were conducted in a quarternary system containing N, P, and K in a mass ratio of 1:0.4:1, where N consisted of 50% each of  $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N. The stock solution was produced by dissolving ammonium nitrate ( $\text{NH}_4\text{NO}_3$ , Chemical Abstracts Service (CAS) number 6484-52-2, Merck) and water-free dipotassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4$ , CAS number 7758-11-4, Merck) in millipore water with an EC of  $< 0.055 \mu\text{S cm}^{-1}$ . Nomenclature of the samples referred to the assumed annual average (AVG) fertiliser input of  $200 \text{ kg N ha}^{-1}$ , set as 1 AVG. The 1 AVG NPK solution had a pH of 7.7 and an EC of  $100.1 \mu\text{S cm}^{-1}$ . The six applied batch equilibrium concentrations were adapted to this annual average; consequently, 2 AVG referred to  $400 \text{ kg N ha}^{-1}$ , 0.5 AVG to  $100 \text{ kg N ha}^{-1}$ . All concentrations are displayed in Table 3. Hence, the concentrations of the calculated target nutrient solutions applied in the batch experiment ranged from  $3.1 \text{ mg L}^{-1}$  (0.25 AVG) to  $50 \text{ mg L}^{-1}$  (4 AVG) for N and K, corresponding to  $1.6 \text{ mg L}^{-1}$  and  $25 \text{ mg L}^{-1}$   $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N, and  $1.2 \text{ mg L}^{-1}$  to  $19.8 \text{ mg L}^{-1}$   $\text{PO}_4^{3-}$ -P.

Prior to conduction of the batch experiments, all vessels and devices used were rinsed in a 0.1 M HCl acid bath. Exactly 10 g of substrate was weighed into 100 mL Duran GL 45 borosilicate glass vessels in five replicates for the variants with only millipore water (0 AVG) and in triplicate for the treatments with addition of NPK solution (0.25 AVG, 0.5 AVG, 1 AVG, 2 AVG, 4 AVG). Also, controls with no soil but only the NPK solution ( $C_0$ ) were set up in five replicates. These initial NPK concentrations were used as a reference value to calculate the sorbed amount of nutrients. According to OECD guideline

106, the samples were pre-equilibrated at room temperature overnight in 45 mL millipore water (13 to 21 h) on an orbital shaker (KS 501 D, IKA, Staufen, Germany) at 130 rpm. After pre-equilibration, 5 mL of tenfold-concentrated NPK solution was added to reach the target concentration and soil/solution ratio of 1:5 (w/v) (10 g soil, 50 mL solution). This suspension was equilibrated for 24 h on an end-over-end shaker at 10 rpm. After shaking, the suspension was allowed to sediment for 5 to 10 min. Then, it was filtrated in a slow-draining NPK-free folded filter, grade 131, 125 mm diameter of Munktell, Bärenstein, Germany, which was rinsed with 100 mL of millipore water before use. This pre-filtrate was discarded. All filtrates were ultracentrifugated (Optima L-90K, rotor 45Ti, Beckmann Coulter, Krefeld, Germany) for 20 min at 39,000 rpm and  $10^\circ\text{C}$  to match the preconditions in cleanliness of particles for instrumental analysis. After this step, all samples were frozen at  $-18^\circ\text{C}$  until further analysis. As the preconditions for particle-free samples were not fulfilled by ultracentrifugation, all thawed samples were filtered in a  $0.45 \mu\text{m}$  glass fibre syringe pre-filter (Sartorius, Göttingen, Germany) before being analysed. Due to its low stability in aqueous solutions,  $\text{NH}_4^+$ -N was analysed promptly after thawing the samples to minimise the risk of volatilisation losses.

### 2.4 Derivation of sorption isotherms according to Freundlich and to Langmuir

The nutrient concentrations in the aqueous phase and the initial concentrations of the NPK solution without substrate were analysed, and the nutrient concentrations of the solid phase were calculated using the following equation:

$$C_s = \frac{v}{m} \times (C_0 - C_w), \tag{1}$$

where  $C_s$  represents the calculated amount of nutrients in the solid phase at equilibrium ( $\text{mg kg}^{-1}$ ),  $v$  refers to the volume of the solution (L),  $m$  to the mass of the substrate (kg),  $C_0$  is the initial nutrient concentration of the NPK solution without substrate ( $\text{mg L}^{-1}$ ), and  $C_w$  is the analysed nutrient concentration in the aqueous phase after 24 h of equilibration ( $\text{mg L}^{-1}$ ).

**Table 3** Applied batch equilibrium concentrations (0 AVG–4 AVG) and corresponding annual fertilisation schemes for  $\text{N}_{\text{total}}$ ,  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N,  $\text{PO}_4^{3-}$ -P, and  $\text{K}^+$

Concentrations	$\text{N}_{\text{total}}$ ( $\text{kg ha}^{-1}$ )	$\text{NH}_4^+$ -N ( $\text{kg ha}^{-1}$ )	$\text{NO}_3^-$ -N ( $\text{kg ha}^{-1}$ )	$\text{PO}_4^{3-}$ -P ( $\text{kg ha}^{-1}$ )	$\text{K}^+$ ( $\text{kg ha}^{-1}$ )
0 AVG	0	0	0	0	0
0.25 AVG	50	25	25	19.8	50
0.5 AVG	100	50	50	39.6	100
1 AVG	200	100	100	79.2	200
2 AVG	400	200	200	158.4	400
4 AVG	800	400	400	316.8	800

As most substrates contained water-soluble nutrients, release of nutrients into the equilibrium solution occurred, so the initial nutrient concentrations without addition of NPK were not zero. In several cases, this led to a greater  $C_w$  than  $C_0$ , which resulted in negative values for the calculated  $C_s$ . Hence, the dimensionless term  $a$  was added to the Freundlich and Langmuir equations to display the intersection of the isotherm with the y-axis, indicating the initial concentration of the water-soluble fraction of a nutrient in the substrate. For describing nutrient sorption on the different materials, two adsorption isotherm equations were applied:

Freundlich:

$$C_s = a + K_f \times C_w^n, \tag{2}$$

Langmuir:

$$C_s = a + \frac{K_l \times q_{max} \times C_w}{1 + K_l \times C_w}, \tag{3}$$

where  $C_s$  represents the amount of nutrient removed at equilibrium ( $\text{mg kg}^{-1}$ ),  $a$  displays the additional term to display the initial concentration of the water-soluble fraction of a nutrient in the substrate,  $K_f$  is the Freundlich affinity coefficient ( $\text{mg}^{(1-n)} \text{L}^{-n} \text{g}^{-1}$ ),  $C_w$  is the equilibrium concentration of the sorbate in solution ( $\text{mg L}^{-1}$ ),  $n$  is the Freundlich linearity constant,  $K_l$  represents the Langmuir bonding term related to interaction energies ( $\text{L mg}^{-1}$ ), and  $q_{max}$  is the Langmuir maximum adsorption capacity ( $\text{mg kg}^{-1}$ ). All sorption isotherms were calculated by using the open source Linux-based software QtiPlot (Version 0.9.9-rc10).

All isotherms were derived from six different NPK concentrations (0 AVG, 0.25 AVG, 0.5 AVG, 1 AVG, 2 AVG, 4 AVG), with the exception of the isotherms of  $\text{NH}_4^+\text{-N}$  to clay. Due to inconsistencies with the sample preparation,

the sorption data of 1 AVG and 2 AVG for  $\text{NH}_4^+\text{-N}$  had to be discarded. Therefore, the sorption isotherms of  $\text{NH}_4^+\text{-N}$  were only derived from four different NPK concentrations (0 AVG, 0.25 AVG, 0.5 AVG, 4 AVG).

### 2.5 Calculation of relative difference of initial and final NPK concentrations in solution

In addition to the sorption isotherms, the relative differences (RD) were calculated for all substrate mixtures and NPK solution concentrations using the following equation:

$$RD = \frac{(C_0 - C_w) \times 100}{C_0}, \tag{4}$$

where  $RD$  displays the relative difference between  $C_w$  and  $C_0$  [%],  $C_w$  is the final nutrient concentration in solution ( $\text{mg L}^{-1}$ ), and  $C_0$  the initial concentration of the NPK solution without substrate ( $\text{mg L}^{-1}$ ). RD values above 0 indicate sorption, an RD of 100% means that all available nutrients were sorbed by the substrate, whereas RD values below zero indicate release of water-soluble nutrients from the substrate into the solution.

## 3 Results

### 3.1 Sorption of $\text{NH}_4^+\text{-N}$

#### 3.1.1 $\text{NH}_4^+\text{-N}$ sorption on biochar

Release of  $\text{NH}_4^+\text{-N}$  from biochar (100B) equilibrated in millipore water for 24 h was low, with only  $0.5 \text{ mg kg}^{-1}$ . In contrast, release from the Arenosol was almost eightfold higher (Table 4). An increasing share of biochar in the substrate

**Table 4** Nutrients released from the solid phase ( $C_s$ ) of the Arenosol, biochar (B), clay (C), and their mixtures into aqueous solution after 24 h of shaking in millipore water without addition of NPK solution (0 AVG;  $n = 5$ )

Substrate sample	Description	$\text{NH}_4^+\text{-N}$ ( $\text{mg kg}^{-1}$ )	$\text{NO}_3^-\text{-N}$ ( $\text{mg kg}^{-1}$ )	$\text{K}^+$ ( $\text{mg kg}^{-1}$ )	$\text{PO}_4^{3-}\text{-P}$ ( $\text{mg kg}^{-1}$ )
0B/0C	Arenosol	3.9	27.1	13.8	0.6
1B	1% biochar	3.3	12.8	22.5	0.3
2.5B	2.5% biochar	3.4	7.2	39.0	0.7
5B	5% biochar	2.4	5.8	81.8	0.6
10B	10% biochar	0.7	4.1	177.8	0.8
100B	100% biochar	0.5	3.1	1734.4	24.5
1C	1% clay	4.1	2.6	17.2	0.1
2.5C	2.5% clay	4.0	2.7	22.2	0.0
5C	5% clay	3.4	3.1	20.2	0.0
10C	10% clay	2.6	4.3	23.1	0.0
100C	100% clay	1.7	19.0	27.9	0.0

The second column indicates the percentage (w/w) of biochar or clay in the substrate mixture. Concentrations above 0 indicate release of water-soluble nutrients from the substrate

decreased the amount of  $\text{NH}_4^+$ -N being dissolved. No  $\text{NH}_4^+$ -N release occurred for any substrate mixture that received the NPK solution (Fig. 3a). The Freundlich model described the  $\text{NH}_4^+$ -N sorption to biochar better for the unamended Arenosol and all biochar-Arenosol mixtures ( $R^2$  0.96 to 0.99; Table 5), whereas the sorption to biochar itself was better described by the Langmuir model ( $R^2 = 0.68$ ). As displayed in Figs. 1a and 3a, the addition of lower doses of biochar to sandy soil had no effects on sorption or even decreased  $\text{NH}_4^+$ -N sorption. When compared with the unamended Arenosol (0B/0C), the addition of 1%, 2.5%, 5% did not show any effect. Only the addition of 10% and 100% showed an increase of  $\text{NH}_4^+$ -N sorption to 27.6% and 86.2%, respectively, when compared to  $C_0$  at the highest added NPK concentration (4 AVG).

### 3.1.2 $\text{NH}_4^+$ -N sorption on clay

Clay released only the very low amount of 1.7 mg  $\text{NH}_4^+$ -N  $\text{kg}^{-1}$  for 100C (Table 4); a larger amount of clay also decreased release of  $\text{NH}_4^+$ -N. Only marginal release occurred for the substrate mixtures with a low share of clay (1C, 2.5C) that received the NPK solution (Fig. 3b). Half of the isotherms were better described by the Freundlich model (0C, 2.5C, 5C) than by Langmuir (1C, 10C, 100C), whereas the differences were marginal. It is noticeable that the maximal sorption capacity ( $q_{max} = 51.8 \text{ mg kg}^{-1}$ ) of the Arenosol decreased when 1% clay was added ( $q_{max} = 27.9 \text{ mg kg}^{-1}$ ). Addition of 2.5% and 5% clay also evoked only marginal effects. Starting from 10%, clay addition showed a visible effect of increased  $\text{NH}_4^+$ -N sorption ( $q_{max} = 97.6 \text{ mg kg}^{-1}$ ). However, due to loss of experimental data (as described in Sect. 2.4), the results of this treatment are not based on the five test substance concentrations recommended by OECD guideline 106 (OECD 2000), hence their validity may be limited compared to the other treatments in this study.

## 3.2 Sorption of $\text{NO}_3^-$ -N

### 3.2.1 $\text{NO}_3^-$ -N sorption on biochar

Unamended Arenosol showed the greatest  $\text{NO}_3^-$ -N release of 27.1 mg  $\text{kg}^{-1}$ . Addition of biochar subsequently reduced  $\text{NO}_3^-$ -N release to only 3.1 mg  $\text{kg}^{-1}$  for the biochar (Table 4). The Langmuir model could not be applied to any of the sandy mixtures for  $\text{NO}_3^-$ -N, only to 100B ( $R^2 = 0.87$ ). For the unamended Arenosol, no sorption model could be applied at all. In contrast, the Freundlich model could be applied to all substrate mixtures. The  $R^2$  for Freundlich ranged from only 0.64 (1B) to 0.86 (100B), with the

Freundlich linearity constant ( $n$ ) being above 1, resulting in convex isotherms (see Fig. 1c). Only the addition of the highest NPK concentration (4 AVG) led to sorption of  $\text{NO}_3^-$ -N to the unamended Arenosol and all Arenosol mixtures (Figs. 1c, 3c). Only the biochar itself did not release  $\text{NO}_3^-$ -N and had a  $q_{max}$  of 183.9 mg  $\text{kg}^{-1}$ . All other concentrations provoked release of  $\text{NO}_3^-$ -N. However, as displayed in Fig. 3c,  $\text{NO}_3^-$ -N release was highest in the unamended Arenosol; the larger the amount of biochar present in the substrate, the less  $\text{NO}_3^-$ -N was released. With the addition of higher NPK concentrations,  $\text{NO}_3^-$ -N release diminished, as indicated by less negative RD values. On the other hand, the RD for biochar decreased from 98.5% (0.25 AVG) to 47.7% (4 AVG), indicating that the maximum sorption capacity of the biochar mixture was already reached.

### 3.2.2 $\text{NO}_3^-$ -N sorption on clay

In contrast to biochar, addition of clay led to greater  $\text{NO}_3^-$ -N release rates compared to the unamended Arenosol, up to 19 mg  $\text{kg}^{-1}$  for the clay itself (Table 4). A Freundlich isotherm could only be derived for the unamended Arenosol, whereas the creation of Langmuir isotherms was not possible. However, the very low  $R^2$  of 0.002 indicated no relation between sorbate and sorbent. Release of  $\text{NO}_3^-$ -N was observed up to 30.1 mg  $\text{kg}^{-1}$  for clay itself at the highest NPK concentration (4 AVG). Even though this was the greatest amount released, the RD compared to the initial  $\text{NO}_3^-$ -N content decreased to  $-20.5\%$  (Fig. 3d). For the lowest NPK dose (0.25 AVG; data not shown), the RD was as large as  $-320\%$ , indicating more than three times as much  $\text{NO}_3^-$ -N release as initially added to the 100C substrate.

## 3.3 Sorption of $\text{K}^+$

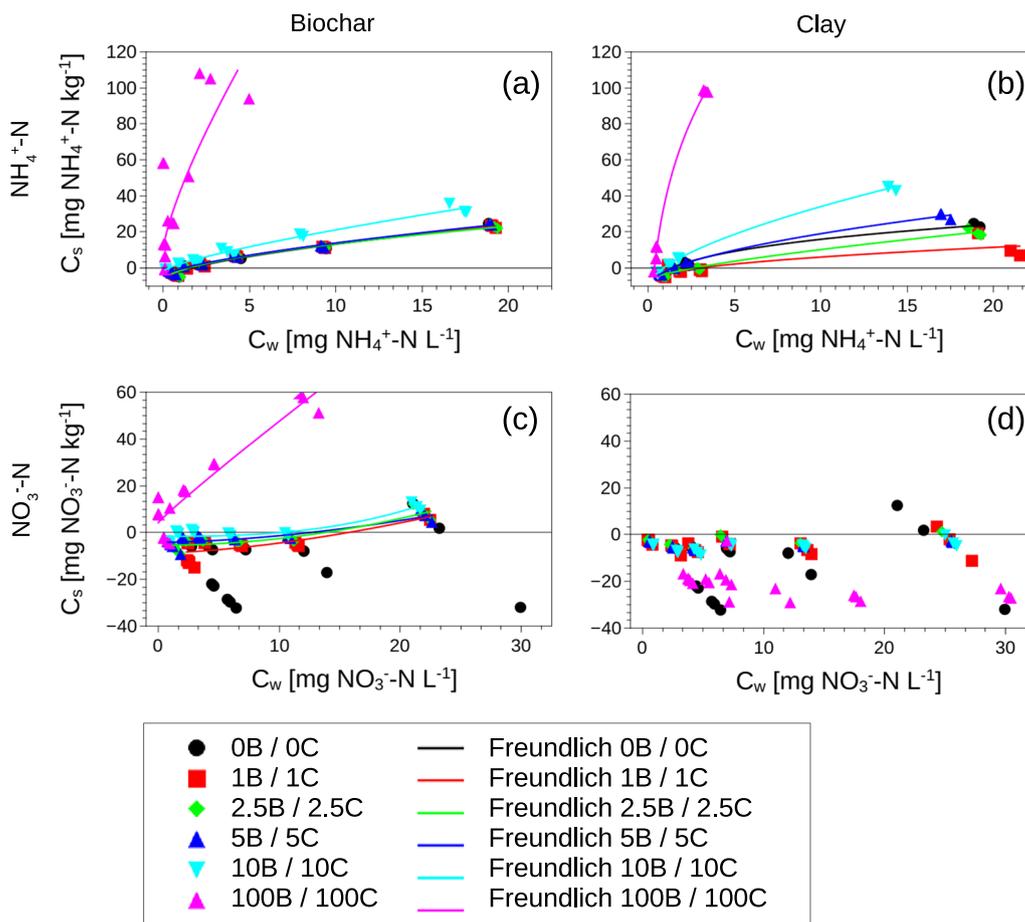
### 3.3.1 $\text{K}^+$ sorption on biochar

All mixtures, including the ones that received no NPK solution, showed release of  $\text{K}^+$ . The unamended Arenosol released 13.8 mg  $\text{K}^+$   $\text{kg}^{-1}$ . With greater biochar share,  $\text{K}^+$  release significantly increased up to 1734.4 mg  $\text{kg}^{-1}$  (Table 4). The  $R^2$  was greater for Freundlich models of 0B, 1B, and 2.5B (up to 0.99); for 5B and 10B, the Langmuir model fitted better, with  $R^2$  decreasing to only 0.12 for 10B. The  $\text{K}^+$  release from the biochar itself could not be described by any of the models. Biochar showed very strong  $\text{K}^+$  release of up to almost 400 mg  $\text{kg}^{-1}$  for the highest NPK concentration added (4 AVG; data not shown). Figure 2a shows the clear relation of biochar share and the increase of  $\text{K}^+$  release: for the unamended Arenosol, the two highest NPK concentrations led to sorption of  $\text{K}^+$ , whereas the addition of lower doses only released  $\text{K}^+$ . The addition of 1% biochar to the

**Table 5** Sorption parameters of Freundlich and Langmuir adsorption isotherms for NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N, K<sup>+</sup>, and PO<sub>4</sub><sup>3-</sup>-P to the unamended Arenosol (0B/0C), biochar (100B), clay (100C), and their mixtures

Substrate sample	Freundlich					Langmuir				
	<i>a</i>	<i>K<sub>f</sub></i> (mg <sup>(1-n)</sup> L <sup>-n</sup> g <sup>-1</sup> )	<i>n</i>	<i>R</i> <sup>2</sup>	STDV	<i>a</i>	<i>K<sub>l</sub></i> (L mg <sup>-1</sup> )	<i>q<sub>max</sub></i> (mg kg <sup>-1</sup> )	<i>R</i> <sup>2</sup>	STDV
<b>NH<sub>4</sub><sup>+</sup>-N</b>										
0B/0C	- 6.19	4.595	0.625	0.961	1.748	- 3.50	0.029	75.033	0.954	1.897
1B	- 7.25	5.790	0.560	0.985	1.185	- 3.94	0.046	57.469	0.979	1.395
2.5B	- 6.34	5.081	0.587	0.977	1.423	- 3.54	0.041	59.191	0.972	1.569
5B	- 4.16	3.743	0.682	0.987	1.084	- 2.62	0.031	71.317	0.984	1.205
10B	- 1.55	3.874	0.768	0.981	1.709	- 0.87	0.029	100.411	0.982	1.657
100B	10.67	32.565	0.762	0.636	23.200	9.66	0.299	172.690	0.681	21.700
1C	- 7.47	4.409	0.486	0.785	3.433	- 5.01	0.073	27.902	0.792	3.381
2.5C	- 6.36	3.207	0.713	0.981	1.441	- 5.28	0.034	63.372	0.981	1.441
5C	- 9.98	8.274	0.545	0.993	1.167	- 6.37	0.080	60.948	0.993	1.156
10C	- 9.27	10.121	0.632	0.998	0.975	- 6.35	0.077	97.580	0.998	0.885
100C	- 122.13	160.690	0.263	0.998	2.117	- 38.48	0.691	196.223	0.998	1.991
<b>NO<sub>3</sub><sup>-</sup>-N</b>										
0B/0C	- 13.02	0.216	0.728	0.002	12.798	n.d.	n.d.	n.d.	n.d.	n.d.
1B	- 8.69	0.105	1.603	0.631	3.706	n.d.	n.d.	n.d.	n.d.	n.d.
2.5B	- 5.46	0.030	1.982	0.838	2.236	n.d.	n.d.	n.d.	n.d.	n.d.
5B	- 4.15	0.053	1.726	0.802	2.031	n.d.	n.d.	n.d.	n.d.	n.d.
10B	- 1.63	0.003	2.738	0.842	2.071	n.d.	n.d.	n.d.	n.d.	n.d.
100B	4.21	4.980	0.940	0.859	7.829	3.29	0.033	183.891	0.867	7.602
1C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2.5C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
100C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>K<sup>+</sup></b>										
0B/0C	- 20.18	3.404	0.754	0.987	1.962	- 17.46	0.009	190.048	0.987	1.988
1B	- 36.06	6.180	0.595	0.981	2.102	- 28.52	0.014	134.467	0.979	2.206
2.5B	- 40.82	0.223	1.342	0.933	3.256	n.d.	n.d.	n.d.	n.d.	n.d.
5B	- 104.34	7.735	0.486	0.575	7.800	- 93.04	0.015	93.785	0.579	7.768
10B	- 452.29	208.991	0.094	0.119	21.668	- 204.94	0.018	116.322	0.120	21.645
100B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1C	- 26.51	4.882	0.475	0.864	3.036	- 21.32	0.025	46.095	0.869	2.975
2.5C	- 20.04	0.071	1.771	0.863	7.022	n.d.	n.d.	n.d.	n.d.	n.d.
5C	- 26.00	1.048	1.195	0.993	2.140	n.d.	n.d.	n.d.	n.d.	n.d.
10C	- 36.08	2.186	1.152	0.996	2.257	n.d.	n.d.	n.d.	n.d.	n.d.
100C	- 96.74	6.137	1.412	0.996	4.473	n.d.	n.d.	n.d.	n.d.	n.d.
<b>PO<sub>4</sub><sup>3-</sup>-P</b>										
0B/0C	- 26.51	33.172	0.115	0.994	0.561	- 1.28	0.516	21.718	0.975	1.165
1B	- 4.95	10.796	0.315	0.994	0.521	- 0.25	0.275	24.674	0.984	0.970
2.5B	- 4.68	9.732	0.367	0.981	1.118	- 0.48	0.205	28.277	0.970	1.415
5B	- 9.55	15.699	0.262	0.996	0.544	- 1.10	0.311	27.354	0.987	0.954
10B	- 13.41	20.132	0.242	0.985	1.184	- 1.58	0.324	30.923	0.973	1.564
100B	- 21.51	0.016	2.427	0.563	6.491	n.d.	n.d.	n.d.	n.d.	n.d.
1C	- 2.87	16.705	0.347	0.986	1.568	0.65	0.543	38.709	0.992	1.236
2.5C	- 1.27	16.046	0.429	0.987	1.795	0.72	0.388	49.846	0.995	1.136
5C	- 0.54	18.010	0.461	0.991	1.743	1.37	0.349	60.766	0.991	1.724
10C	- 0.27	20.530	0.511	0.995	1.491	2.10	0.276	79.860	0.988	2.255
100C	4.55	91.896	0.690	0.986	3.858	4.82	1.016	176.397	0.985	3.942

The numbers for the substrate samples refer to the percentage (w/w) of the biochar (B) or clay (C) addition to the Arenosol. Values are shown for the intersection of the isotherm with the y-axis (*a*), Freundlich affinity coefficient (*K<sub>f</sub>*), Freundlich linearity constant (*n*), the Langmuir bonding term (*K<sub>l</sub>*), Langmuir maximum adsorption capacity (*q<sub>max</sub>*), coefficients of determination (*R*<sup>2</sup>), and standard deviations of the respective isotherms (STDV). In several cases, no sorption isotherms could be determined (n.d.)



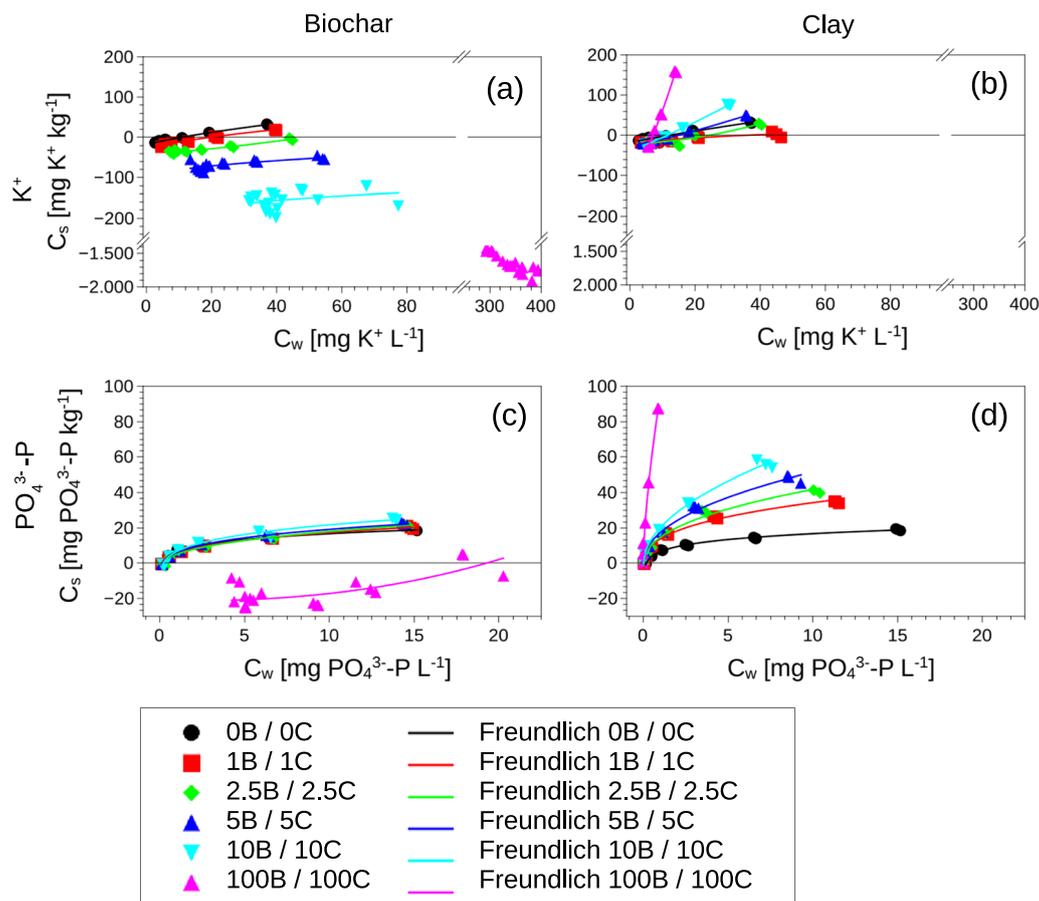
**Fig. 1** Measured nutrient concentrations in the aqueous solutions ( $C_w$ ) and calculated nutrient concentrations in the substrates ( $C_s$ ) for  $\text{NH}_4^+\text{-N}$  (top row: **a**, **b**) and  $\text{NO}_3^-\text{-N}$  (bottom row: **c**, **d**), and for substrates with biochar (left side: **a**, **c**) and clay share (right side: **b**, **d**). 0B/0C refers to the unamended Arenosol, 100B to the biochar itself, and 100C to the clay. Symbols, lines, and colours are explained in the legend box below the figures. The numbers in the legend indi-

cate the percentage (w/w) of biochar (B) or clay (C) addition to the Arenosol. Data points below the x-axis indicate nutrient release; data points above indicate nutrient sorption to the substrate. Adsorption isotherms according to Freundlich were applied if possible. Due to loss of data, the  $\text{NH}_4^+\text{-N}$  sorption isotherms for clay were only derived from four different NPK concentrations instead of six. For details, see Sect. 2.4

Arenosol resulted in greater  $\text{K}^+$  release, but also showed some sorption for the highest NPK dose. The Arenosol–biochar mixtures with 2.5%, 5%, and 10% biochar exclusively showed  $\text{K}^+$  release. The increase of  $\text{K}^+$  release responded to the share of biochar in the mixture. However, when set in relation to  $C_0$ , all mixtures showed a release of  $\text{K}^+$  (Fig. 3e). The addition of biochar clearly led to a strong increase of  $\text{K}^+$  release, with the biochar itself evoking  $\text{K}^+$  release up to 4000 times the amount of  $\text{K}^+$  added at the lowest addition of NPK solution (0.25 AVG). The RD decreased with increasing NPK concentration to eight times the amount of  $\text{K}^+$  released for 4 AVG.

### 3.3.2 $\text{K}^+$ sorption on clay

All clay mixtures showed medium  $\text{K}^+$  release of  $17.2 \text{ mg kg}^{-1}$  (1C) to  $27.9 \text{ mg kg}^{-1}$  (100C; Table 4). The Freundlich model described all mixtures better than Langmuir;  $R^2$  values were high, between 0.86 and 0.99. The isotherms of 0C and 1C had an  $n$  of below 1, whereas the others showed a convex form with  $n$  above 1. When low concentrations of NPK were added,  $\text{K}^+$  was only released for the two highest concentrations applied (2 AVG and 4 AVG); all isotherms showed sorption (Figs. 2a and 3e). These figures also showed that for 1C and 2.5C, sorption decreased compared to the



**Fig. 2** Measured nutrient concentrations in the aqueous solutions ( $C_w$ ) and calculated nutrient concentrations in the substrates ( $C_s$ ) for  $K^+$  (top row: **a**, **b**) and  $PO_4^{3--}P$  (bottom row: **c**, **d**), and for substrates with biochar (left side: **a**, **c**) and clay share (right side: **b**, **d**). 0B/0C refers to the unamended Arenosol, 100B to the biochar itself, and 100C to the clay. Symbols, lines, and colours are explained in the legend box below the figures. The numbers in the legend indi-

cate the percentage (w/w) of biochar (B) or clay (C) addition to the Arenosol. Data points below the x-axis indicate nutrient release; data points above indicate nutrient sorption to the substrate. Adsorption isotherms according to Freundlich were applied if possible. Due to strong  $K^+$  release, axis breaks of x- and y-axis were applied for (**a**) and (**b**)

unamended Arenosol. In contrast, clay addition to the Arenosol above 5% increased  $K^+$  sorption of the Arenosol. A steep isotherm with  $n$  of 6.1 indicated strong sorption of  $K^+$  to the clay itself.

### 3.4 Sorption of $PO_4^{3--}P$

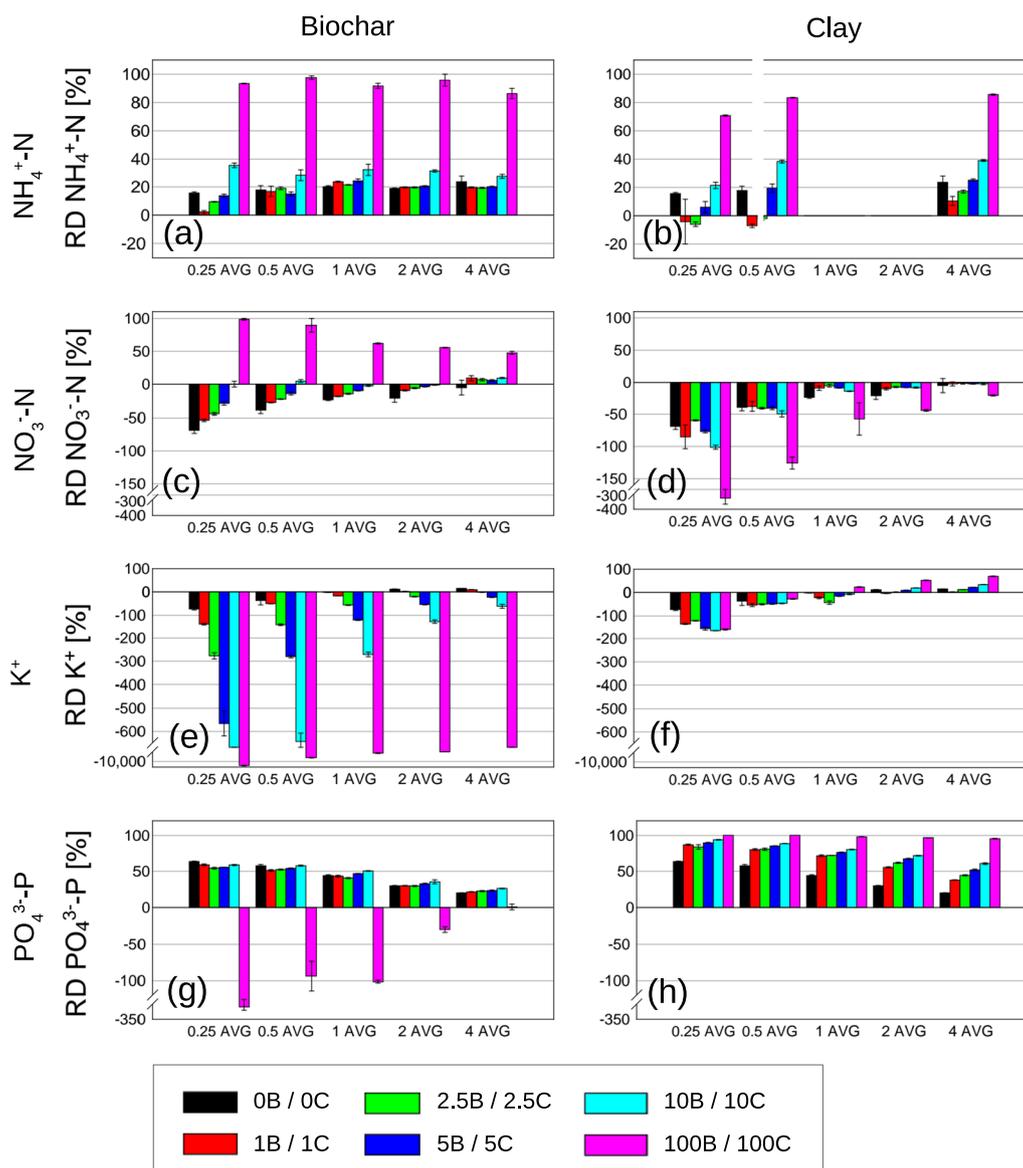
#### 3.4.1 $PO_4^{3--}P$ sorption on biochar

The unamended Arenosol and its mixtures with biochar only released very low amounts of  $PO_4^{3--}P$ , up to  $0.8 \text{ mg kg}^{-1}$ , whereas the plain biochar showed around 30 times more  $PO_4^{3--}P$  release (Table 4). The biochar only provoked release of  $PO_4^{3--}P$ ; no sorption model could be applied. For all other substrates, Freundlich described the sorption best ( $R^2$  of 0.98 and 0.99, respectively). When compared to initial  $PO_4^{3--}P$  concentrations added, the  $PO_4^{3--}P$  release

decreased from more than 300% (0.25 AVG) to slight sorption of 0.9% for 4 AVG (Fig. 3g). Figs. 2c and 3g show that more biochar addition led to gradually greater  $PO_4^{3--}P$  sorption. However, the differences were marginal; when displayed with the Langmuir model, the initial  $q_{max}$  of the Arenosol ( $21.7 \text{ mg kg}^{-1}$ ) slightly increased to  $24.7 \text{ mg kg}^{-1}$  (1B), and finally to  $30.9 \text{ mg kg}^{-1}$  for 10B, not indicating a great increase.

#### 3.4.2 $PO_4^{3--}P$ sorption on clay

All mixtures containing clay without NPK addition showed no  $PO_4^{3--}P$  release at all (Table 4). With the exception of 2.5C, the Freundlich model explained the sorption of  $PO_4^{3--}P$  to clay best. All  $R^2$  values were high (0.99). All substrates showed only low or no  $PO_4^{3--}P$  release, but



**Fig. 3** Relative difference (RD) of the nutrient concentration in the aqueous phase ( $C_w$ ) compared to the initial concentration of the NPK solution ( $C_0$ ) for samples with addition of NPK solution. Colours are explained in the legend box below the figures. The diagrams show RD values for the different concentrations of the NPK solution (0.25 AVG, 0.5 AVG, 1 AVG, 2 AVG, 4 AVG), nutrients (from top to bottom: **a, b**:  $\text{NH}_4^+\text{-N}$ ; **c, d**:  $\text{NO}_3^-\text{-N}$ ; **e, f**:  $\text{K}^+$ ; **g, h**:  $\text{PO}_4^{3-}\text{-P}$ ), and different shares of biochar (left side) and clay (right side) in the substrates (0B/0C = unamended Arenosol; 1B/1C = 1% (w/w) biochar

or clay addition, 2.5B/2.5C = 2.5% biochar or clay; 5B/5C = 5% biochar or clay; 10B/10C = 10% biochar or clay; 100B = 100% biochar; 100C = 100% clay). Data points below the x-axis ( $x = 0$ ) indicate nutrient release; data points above indicate nutrient sorption to the substrate. Error bars display the standard error. Due to loss of data, the RD of 1 AVG and 2 AVG cannot be displayed in diagram (b); for details, see Sect. 2.4. For  $\text{NO}_3^-\text{-N}$ ,  $\text{K}^+$ , and  $\text{PO}_4^{3-}\text{-P}$ , axis breaks of the y-axis were applied

sorption. When clay was added,  $\text{PO}_4^{3-}\text{-P}$  sorption increased gradually (Fig. 2d). For Langmuir, there was an increase of  $q_{max}$  from 21.7 (0C) to 38.7 (1C) and 49.8 (2.5C), up to a  $q_{max}$  of 176.4  $\text{mg kg}^{-1}$  for 100C. The sorption isotherm of 100C was the steepest. In relation to the initially added NPK concentration, the relative difference of the equilibrium concentration for the 100C remained very high at

above 95% (Fig. 3h). However, the sorption capacity for the clay–Arenosol mixtures was already decreasing, indicating that they had already reached their sorption capacity. As the majority of isotherms were better described by Freundlich than by the Langmuir model, indicated by greater coefficient of determination ( $R^2$ ; see Table 5), all

sorption isotherms displayed in this study were derived by the Freundlich equation (Figs. 1 and 2).

## 4 Discussion

The nutrient adsorption of most substrates and substrate mixtures in our study was better described by Freundlich than by the Langmuir model, in particular for the unamended Arenosol, the clay itself, most Arenosol–clay mixtures, and the Arenosol–biochar mixtures up to 5% biochar addition. This implies that in these cases most multisite adsorption occurred on heterogeneous surfaces (Freundlich) rather than monolayer adsorption with no interactions between the adsorbed molecules (Langmuir) (e.g., Limousin et al. 2007; Oliveira et al. 2017; Rens et al. 2018; Yao et al. 2013). The latter may apply for mixtures with 10% biochar addition and for the biochar itself, where  $R^2$  of the Langmuir isotherm is greater than that of the Freundlich model (see Table 5). However, the differences in  $R^2$  between both adsorption models remain very low.

### 4.1 Sorption of $\text{NH}_4^+\text{-N}$

#### 4.1.1 $\text{NH}_4^+\text{-N}$ sorption on biochar

The presence of biochar in the Arenosol showed no effects or even decreased the maximum sorption capacity  $q_{max}$  for the lower doses < 10% but increased  $q_{max}$  by 34% for 10B and 130% for 100B. Only a small number of studies conducted batch experiments with mixtures of soil and biochar, most of them reporting only marginal or no effects on  $\text{NH}_4^+\text{-N}$  sorption. Gronwald et al. (2015), for example, found a slight increase of  $\text{NH}_4^+\text{-N}$  sorption of a sandy loam after addition of biochars made of woodchips (up to 8%) and digestate (up to 17%). The addition of the same biochars to a silty loam showed no effects or even resulted in  $\text{NH}_4^+\text{-N}$  release. Rens et al. (2018) reported similar findings: a slight but significant increase of  $\text{NH}_4^+\text{-N}$  sorption after application of a woody mid-temperature biochar to a sandy soil at lower  $\text{NH}_4^+\text{-N}$  concentration of the nutrient solution added. However, the same biochar significantly decreased  $\text{NH}_4^+\text{-N}$  sorption with greater biochar addition when added to a silty clay loam soil. Alling et al. (2014) found no significant changes in  $\text{NH}_4^+\text{-N}$  concentration after addition of a woody low-temperature biochar to seven acidic tropical peat and mineral soils. These results are in line with our findings for biochar-soil mixtures. Most batch equilibrium experiments were conducted with pure biochar and showed significant sorption of  $\text{NH}_4^+\text{-N}$  (e.g., Aghoghovwia et al. 2020; Cui et al. 2016; Fidel et al. 2018; Li et al. 2018; Liu et al. 2016; Zheng et al. 2018).

Takaya et al. (2016), for example, revealed 10% to 13% sorption of  $\text{NH}_4^+\text{-N}$  in the initial nutrient solution for biochars from different feedstocks with pyrolysis temperatures between 400 and 650 °C. Several authors reported increasing  $\text{NH}_4^+\text{-N}$  sorption capacity with decreasing pyrolysis temperature, with maximum sorption capacities for low-temperature biochars at pyrolysis temperatures below 400 °C (e.g., Li et al. 2018; Zheng et al. 2013). The  $q_{max}$  of our biochar, produced at approx. 450 °C, is 172.7 mg kg<sup>-1</sup> and rather low.

Surface complexation of the nutrient with negatively charged oxygen-containing functional groups like carboxyl and carbonyl is an important mechanism for  $\text{NH}_4^+$  sorption to biochar surfaces (e.g., Cui et al. 2016; Kizito et al. 2015; Zheng et al. 2013, 2018). With higher pyrolysis temperatures, the total content of O and total amount of acidic oxygen-containing functional groups on the surface of biochars decrease (Zheng et al. 2013), leading to a reduction in negative charge on the biochar surface (Chen et al. 2008). Consequently, less surface complexation and less electrostatic attraction occur, resulting in a decrease of  $\text{NH}_4^+$  sorption with higher pyrolysis temperatures. This explains the higher sorption capacity of low-temperature biochars for  $\text{NH}_4^+$  compared to high-temperature biochars. The negative charge of biochar surfaces leads to electrostatic attraction of the positively charged  $\text{NH}_4^+$ , resulting in cation exchange;  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  may be exchanged by  $\text{NH}_4^+$  (e.g., Cui et al. 2016; Ding et al. 2010; Gai et al. 2014; Li et al. 2018; Zheng et al. 2013, 2018). In contrast, sequestration in pores plays no decisive role for  $\text{NH}_4^+$  adsorption to biochars (e.g., Cui et al. 2016; Zheng et al. 2013). In our study, biochar addition of less than 10% showed no or converse effects, whereas  $\text{NH}_4^+\text{-N}$  sorption to biochar itself sharply increased. This may result from the larger surface area offering more binding sites for  $\text{NH}_4^+\text{-N}$  compared to the Arenosol.

Another effect that may or may not have contributed to the results in this study was  $\text{NH}_3$  volatilisation. As the pH ( $\text{H}_2\text{O}$ ) of the biochar was alkaline (9.1) and the pH of the NPK solution added was relatively neutral (7.7),  $\text{NH}_3$  volatilisation that can occur at pH values above 7 (Sommer et al. 2004) may have taken place. In batch experiments, nutrient sorption to the solid phase is calculated by the difference between initial and final nutrient solution in the aqueous phase; however, the mechanisms behind the nutrient decrease remain unknown. Other processes like decomposition, precipitation, or volatilisation may occur and lead to an overestimation of the actual amount of nutrient sorbed. Hence, we may misinterpret  $\text{NH}_3$  volatilisation as  $\text{NH}_4^+\text{-N}$  “sorption”, in particular for the biochar itself (Fig. 1a). This is in line with Wang et al. (2015a), who assumed  $\text{NH}_3$  volatilisation to be the reason for incomplete recovery of only about 60% of  $\text{NH}_4^+\text{-N}$  after

a batch adsorption experiment with biochar of high pH values. However, as no measures were applied to detect  $\text{NH}_3$  volatilisation, possible  $\text{NH}_3$  volatilisation cannot be excluded, confirmed, or quantified.

#### 4.1.2 $\text{NH}_4^+$ -N sorption on clay

Clay addition also enhanced  $\text{NH}_4^+$ -N sorption of the Arenosol, whereas the maximum sorption capacity ( $q_{max}$ ) of the clay itself was  $196.22 \text{ mg kg}^{-1}$ , 13.6% greater than that for biochar. These results are in line with several studies that reported sorption of  $\text{NH}_4^+$ -N onto clayey material. In a batch experiment using a clayey sediment with 55% calciummontmorillonite content, Baker and Fraij (2010) found  $\text{NH}_4^+$ -N removal rates from aqueous solution up to 45%. Alshameri et al. (2018) evaluated six natural clay minerals for their suitability to remove  $\text{NH}_4^+$ -N from waste water, where vermiculite and montmorillonite showed the highest  $\text{NH}_4^+$ -N maximum adsorption capacities of  $50.06 \text{ mg g}^{-1}$  and  $40.84 \text{ mg g}^{-1}$ , respectively. Kaolinite, in contrast, had a maximum adsorption capacity of  $15.58 \text{ mg g}^{-1}$ ; the Vertisol used in our study contained 20% to 30% Kaolinite. Zhu et al. (2011), who tested a wide range of materials for wetland construction, reported a maximum  $\text{NH}_4^+$ -N adsorption capacity of  $3.33 \text{ mg g}^{-1}$  for the 2:1 clay mineral vermiculite that had a medium shrink-swell capacity. Only two studies were found that conducted batch experiments with  $\text{NH}_4^+$ -N on clayey material as soil amendment. Both studies did not derive sorption isotherms. Dempster et al. (2012) conducted a sorption experiment with clayey subsoil that had a clay content of 60.4% and mainly consisted of kaolinite and quartz. Maximal  $\text{NH}_4^+$ -N sorption from aqueous solution was 32%. Tahir and Marschner (2017) mixed a high-smectite subsoil (73% clay content) and a low-smectite subsoil (42% clay content) with an Arenosol (3% clay content). The addition of 20% (w/w) clayey subsoil led to a 20-fold increase of  $\text{NH}_4^+$ -N sorption for the high-smectite subsoil ( $139 \text{ mg g}^{-1}$ ) and a 14-fold increase for the low-smectite ( $99 \text{ mg g}^{-1}$ ) subsoil.

Several studies claim cation exchange to be the main sorption mechanism for  $\text{NH}_4^+$  to clay (e.g., Alshameri et al. 2018; Zhu et al. 2011). This is a result of the large chemically active surface area, the variable net negative charge, and variable interlayer spacing of the predominant 2:1 smectite clay minerals that account for 40% to 60% of the clay applied in our study. Smectites exhibit a large cation exchange capacity; in our study, the addition of 1% clay increased the initial CEC of the Arenosol of  $0.9 \text{ cmol}_c \text{ kg}^{-1}$  3.8 fold (data not shown). Therefore, we assume cation exchange to be the main mechanism for  $\text{NH}_4^+$ -N sorption on clay in our study. As the pH of the NPK solution in

this batch experiment was 7.7 and the pH ( $\text{H}_2\text{O}$ ) of the clay was 8.0, volatilisation of  $\text{NH}_3$  might have occurred. However, as in the case of biochar mentioned above, this possible mechanism cannot be excluded.

## 4.2 Sorption of $\text{NO}_3^-$ -N

### 4.2.1 $\text{NO}_3^-$ -N sorption on biochar

The Arenosol showed distinct  $\text{NO}_3^-$ -N release that was diminished by increasing biochar share. In contrast, undiluted biochar sorbed  $\text{NO}_3^-$ -N up to a  $q_{max}$  of  $183.89 \text{ mg kg}^{-1}$ . Slightly rising  $K_f$  values with increasing biochar share indicate a marginal increase of  $\text{NO}_3^-$ -N sorption with increasing biochar share. Several studies have tested biochars for their ability to sorb  $\text{NO}_3^-$ . Most studies revealed a close correlation between high pyrolysis temperatures and  $\text{NO}_3^-$  sorption. With production temperatures up to  $550 \text{ }^\circ\text{C}$ , no significant  $\text{NO}_3^-$  sorption on low-temperature biochars could be detected (e.g., Alling et al. 2014; Hale et al. 2013; Hollister et al. 2013; Li et al. 2018; Paramashivam et al. 2016). In contrast, regardless of feedstock, many studies reported  $\text{NO}_3^-$  sorption on high-temperature biochars above  $500 \text{ }^\circ\text{C}$  (e.g., Chintala et al. 2013; Fatima et al. 2021; Fidel et al. 2018; Pratiwi et al. 2016; Yang et al. 2017; Zheng et al. 2013). Maximum  $q_{max}$  values in these studies were  $533.5 \text{ mg kg}^{-1}$  for biochar produced from giant reed at  $600 \text{ }^\circ\text{C}$  (Zheng et al. 2013) and  $785 \text{ mg kg}^{-1}$  for biochar produced from lignin biomass component at  $700 \text{ }^\circ\text{C}$  (Yang et al. 2017). For a Eucalyptus biochar produced at  $600 \text{ }^\circ\text{C}$ , Dempster et al. (2012) reported  $\text{NO}_3^-$ -N removal rates from aqueous solution between 38% at the highest addition rate ( $50 \text{ mg NO}_3^- \text{-NL}^{-1}$ ) and 80% at the lowest addition rate ( $2.5 \text{ mg NO}_3^- \text{-NL}^{-1}$ ). In our study, removal rates for biochar ranged between 98.5% for the lowest added concentration ( $1.6 \text{ mg NO}_3^- \text{-NL}^{-1}$ ) and 47.7% for the highest added concentration ( $25 \text{ mg NO}_3^- \text{-NL}^{-1}$ ). However, all mixtures with less than 10% biochar addition predominantly showed  $\text{NO}_3^-$ -N release. As with most batch equilibrium experiments, our experiments were conducted with fresh and untreated biochars. In consequence, no statements regarding the sorption characteristics of biochar over time can be made.

In general,  $\text{NO}_3^-$  is very weakly retained by most soils due to its great solubility in water and negative charge; it is therefore easily leached (Addiscott 2005). Several factors and mechanisms influence  $\text{NO}_3^-$  sorption on biochars. One factor is the feedstock used for biochar production. Strong variations in adsorption capacities in regard to biochar feedstock were mentioned by Gronwald et al. (2015) and Yang et al. (2017), the latter reporting relatively large  $\text{NO}_3^-$  sorption for biochars made from lignin while biochars from cellulose exhibited only low capacity for  $\text{NO}_3^-$  sorption.

Another important factor that controls most biochar properties and therefore  $\text{NO}_3^-$  sorption is the temperature at which biochar was produced. SSA, pore volume, anion exchange capacity (AEC), and concentration of base functional groups increase with higher pyrolysis temperatures (Al-Wabel et al. 2013). Due to their large SSA and large pore volume, biochars exhibit a high number of potential sorption sites with different properties. Yang et al. (2017) proposed the large SSA of biochars to be the controlling parameter for  $\text{NO}_3^-$  sorption. In accordance, Gronwald et al. (2015) found a pronounced correlation between SSA and  $\text{NO}_3^-$  sorption. A further mechanism that is proposed to contribute to sorption of  $\text{NO}_3^-$  to biochar is capture of dissolved  $\text{NO}_3^-$  in micro- and nano-pores (e.g., Kammann et al. 2015; Knowles et al. 2011; Prendergast-Miller et al. 2014; Zheng et al. 2013). However, this sorption effect may attenuate over time, when dissolved organic matter and mineral particles cover biochar surfaces and clog pores, thus reducing the inner reactive surface (e.g., Eykelbosh et al. 2015; Kanthle et al. 2016; Pignatello et al. 2006; Yang et al. 2017). Physical sorption of  $\text{NO}_3^-$ , based on electrostatic attraction, depends on the presence of positively charged sorption sites, expressed by AEC. Some biochars exhibit significant levels of AEC, which may enhance sorption of anionic nutrients like  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  (Chintala et al. 2014; Lawrinenko and Laird 2015). Biochar AEC increases with higher pyrolysis temperatures and with decreasing pH. Lawrinenko and Laird (2015) assumed that oxonium functional groups contribute to pH-independent AEC. Only a few studies have investigated the AEC contents of biochars. Reported AEC levels differ between 0.60 and 27.76  $\text{cmol}_c \text{ kg}^{-1}$  for a wide range of biochar feedstocks (e.g., Cheng et al. 2008; Inyang et al. 2011; Lawrinenko and Laird 2015; Silber et al. 2010). At neutral soil pH, AEC is predominantly controlled by pyrolysis temperature. Ageing is changing AEC over time, especially in low-temperature biochars. Several authors have discussed the potential role of base functional groups for  $\text{NO}_3^-$  sorption. Higher pyrolysis temperatures promote the formation of base functional groups to which  $\text{NO}_3^-$  is chemically sorbed (Al-Wabel et al. 2013; Fatima et al. 2021; Kameyama et al. 2012). However, in Fourier-transform infrared spectra of various biochar samples, Yang et al. (2017) could not observe obvious base functional groups. The pyrolysis temperature is responsible for biochar properties like SSA, presence of positively charged sorption sites, and the number of base functional groups. We assume that the medium pyrolysis temperature of our woody, lignin-rich biomass feedstock is the reason for the comparably medium sorption capacity for  $\text{NO}_3^-$ -N.

#### 4.2.2 $\text{NO}_3^-$ -N sorption on clay

Other than biochar, clay addition triggered  $\text{NO}_3^-$ -N release and none of the substrate mixtures that contained clay showed any

$\text{NO}_3^-$ -N sorption. This is in line with the few other studies that report no effects of clay amendment to  $\text{NO}_3^-$  retention or even an increase of  $\text{NO}_3^-$  release. In the field experiment related to this study, the addition of clay to an Arenosol had no effect on the leaching of  $\text{NO}_3^-$ -N over the 1.5 years in the unfertilised treatment. In contrast, in the second period (months 8 to 16) the  $\text{NO}_3^-$ -N leaching of the fertilised treatment increased by 57.4% compared to the unamended control (Beusch et al. 2019). In a 20-day lysimeter experiment by Dempster et al. (2012), cumulative  $\text{NO}_3^-$ -N leaching significantly decreased by 16% after the addition of clayey subsoil, mainly containing kaolinite and quartz, to a Sodosol. This may be related to the significant increase of water-holding capacity after the addition of the clay because in a batch equilibrium experiment of the same study, clay exhibited no capacity to sorb  $\text{NO}_3^-$ -N. Abdelwaheb et al. (2019) stated an increase of  $\text{NO}_3^-$  sorption with increasing clay content from  $q_{max}$  of 0.25  $\text{mg g}^{-1}$  for unamended sand to 1.60  $\text{mg g}^{-1}$  for a mixture of sand and clay with a clay content of 30%. In the area of water purification, some studies tested the ability of unmodified natural clay minerals and clayey materials to remove anions like  $\text{NO}_3^-$  or  $\text{PO}_4^{3-}$  from water. Most clays exhibit only low to medium AEC, which results in  $\text{NO}_3^-$  removal between 1 and 16  $\text{mg g}^{-1}$  for clay minerals and < 2  $\text{mg g}^{-1}$  for clayey materials at pH 6 and 7 (Lazaratou et al. 2020).

As reported by Dempster et al. (2012), the addition of clay may enhance the water-holding capacity of a soil and, as a result, retain  $\text{NO}_3^-$  solved in the soil solution and therefore prevent  $\text{NO}_3^-$  leaching. Several other studies also stated an increase of water-holding capacity due to clay amendment (e.g., Al-Omran et al. 2010; Costa et al. 2009; de Lima et al. 1998; Mojid et al. 2010; Sabrah et al. 1993; Suzuki et al. 2007). However, due to electrostatic repulsion of the negatively charged anion  $\text{NO}_3^-$  from the net negative surface charge of clays, no physical adsorption of  $\text{NO}_3^-$  to the clay surface itself or interlayers is expected under neutral pH conditions (Addiscott 2005). When conditions change to acidic, the number of positively charged hydroxyl groups on the surfaces of metal oxides and the edges of silicate clays increase (Lazaratou et al. 2020). Consequently, the AEC increases and allows sorption of  $\text{NO}_3^-$  (Mohanty et al. 2015). Özcan et al. (2005) reported  $\text{NO}_3^-$  removal from an aqueous solution of 23  $\text{mg g}^{-1}$  by a natural sepiolite. In a study by Mohanty et al. (2015), 27.5% of initial  $\text{NO}_3^-$  was adsorbed on clay kaolin; both studies were conducted at pH 2, so they do not reflect the conditions of soils used for agriculture.

### 4.3 Sorption of $\text{K}^+$

#### 4.3.1 $\text{K}^+$ sorption on biochar

Increasing biochar application sharply enhanced the release of  $\text{K}^+$ . Only a few batch equilibrium experiments exist for

the sorption of  $K^+$  on biochars. Rens et al. (2018) report a decrease of  $K^+$  adsorption capacity after biochar addition to a silty clay loam soil, but no effect on a sandy soil. Most studies that examined biochar effects on K reported no sorption or retention but an increase of K release (e.g., Limwikran et al. 2018; Raave et al. 2014; Widowati et al. 2014). In theory, due to its large surface area and net negative charge, biochar exposes many potential binding sites for positively charged nutrients like  $K^+$  and  $NH_4^+$ . Usually, K contents of biochars are relatively large because the original feedstock contains a certain quantity, on average 1% K in plant shoot dry matter (Kirkby and Marschner 2012), which is enriched in the pyrolysis process to a multiple of the initial K content (Al-Wabel et al. 2013). As biochar K is predominantly only weakly bound, large amounts of  $K^+$  are dissolved in the soil solution. In an incubation study by Limwikran et al. (2018), up to 64% of biochar  $K^+$  was soluble in water and up to 75% of this  $K^+$  diffused rapidly into the soil.

Rinsing the biochars beforehand would have removed water-soluble  $K^+$  and decreased the amount of  $K^+$  and other nutrients leached (e.g., Hale et al. 2013); it would also have allowed a better estimation of the sorption capacity of  $K^+$  to biochars. However, the intention of this study was to approach real-life biochar production and field conditions in the tropical north-east of Brazil to the extent possible for the conduction of a batch equilibrium experiment. Washing would not be economically feasible for large amounts of biochar. Also, the fertilising effect of plant-available biochar  $K^+$  in soils is desirable.

#### 4.3.2 $K^+$ sorption on clay

In contrast to biochar, clay addition led to a release of  $K^+$  from the unamended Arenosol, clay, and all mixtures for the lower NPK concentrations added, but increased sorption relative to the initial NPK concentration ( $C_{ini}$ ) for the higher concentrations. Few existing studies deal with K sorption or retention of clayey soil amendments. One batch equilibrium study mixed peat for horticultural use with several clayey materials. In that study by Binner et al. (2017), K sorption was found to be positively correlated with CEC ( $R^2 = 0.84$ ) but not with clay content. Also, the SSA, content of Fe oxides, and smectite content correlated with K sorption. The greatest K adsorption was measured in a smectitic bentonite ( $q_{max} = 5760 \text{ mg kg}^{-1}$ ), which also showed great ability to desorb almost all initially sorbed K. This indicated that sorbed K was not fixed in clay interlayers but remained exchangeable at a higher rate than for illitic or kaolinitic clay. Only two other studies regarding  $K^+$  sorption or retention that used clayey materials to amend soils are known to us. In a 1.5 year leaching study that Beusch et al. (2019) conducted at the field site where the material of

our study has its origin, the addition of the same smectitic clay resulted in a significant decrease of  $K^+$  leaching over two consecutive periods of 8 months, by 51.0% and 45.2%, respectively. Reuter (1994) reported approx. 60% reduction of K leaching in a pot experiment with a sandy soil after 2.4% (w/w) brick clay, mainly containing illite, was added. With the addition of only 0.3% (w/w) bentonite, the same effect could be achieved. The bentonite predominantly contained montmorillonite. This study shows that the sorption of  $K^+$  and other nutrients is largely dependent on the mineral composition of clays.

The clay applied in our study contained 40% to 60% smectites and expansible layer phyllosilicates. The interlayer sites of smectites provide a high number of cation adsorption sites (Sparks and Carski 1985). Besides vermiculites, smectites are the clay minerals with the largest SSA of  $600 \text{ m}^2 \text{ g}^{-1}$  to  $800 \text{ m}^2 \text{ g}^{-1}$  and the largest surface charge, resulting in a high CEC of  $80 \text{ cmol}_c \text{ kg}^{-1}$  to  $150 \text{ cmol}_c \text{ kg}^{-1}$  (Sparks 2003b). We assume these characteristics to be the reason for the increase of  $K^+$  adsorption after the addition of clay to an Arenosol. The release of  $K^+$  to the solutions with no or only small amounts of NPK can be explained by the content of  $288.7 \text{ mg kg}^{-1}$  plant-available K in the clay applied in our study. Soil K is divided into soluble, exchangeable, fixed, and structural K (Sparks and Carski 1985). One portion of plant-available K is water-soluble K in the soil solution and is directly released to the mixing solution; the other portion is exchangeable K, which is only weakly bound to the surface of the clay minerals and can be rapidly exchanged by other cations in the solution (Sparks 1987). K that is released from clays can contribute to the K supply of plants in the soil (Binner et al. 2017).

## 4.4 Sorption of $PO_4^{3-}$ -P

### 4.4.1 $PO_4^{3-}$ -P sorption on biochar

In our study, biochar addition to the Arenosol slightly enhanced maximum  $PO_4^{3-}$ -P sorption capacity, whereas undiluted biochar induced release of  $PO_4^{3-}$ -P. Only a few studies have conducted batch equilibrium experiments and derived sorption isotherms to examine P adsorption on biochars, and a very limited number of studies have worked on P adsorption of biochar-soil mixtures at varying pyrolysis temperatures (e.g., Eduah et al. 2019; Ghodszad et al. 2021). As for other nutrients, most batch experiments were conducted with pure biochars; we only found a few studies that have tested soil/biochar mixtures for their maximum P sorption capacity. Addition of 1% rice husk biochar produced at  $650 \text{ }^\circ\text{C}$  to an Arenosol at neutral pH doubled maximum P sorption capacity  $q_{max}$  to  $203 \text{ mg kg}^{-1}$  (Eduah et al. 2019). P sorption capacity increased with increasing pyrolysis temperature for corn cob and rice husk biochars. In contrast,

biochar addition to two acidic soils, an Acrisol and a Ferralsol with pH (H<sub>2</sub>O) 5.03 and 4.73, decreased P sorption with increasing pyrolysis temperature. These results were confirmed in a study by Ghodszad et al. (2021), who also reported an increase of P sorption with increasing pyrolysis temperature in an alkaline soil (pH 7.4) after addition of 6% wheat straw-derived biochar, but a decrease in two acidic soils (pH 4.6 and 6.0). The biochars in this study were produced at 300 °C and 600 °C. Xu et al. (2014) also reported highest P sorption capacity for an acidic Inceptisol (pH (H<sub>2</sub>O) 3.83) with a  $q_{max}$  of 769 mg kg<sup>-1</sup> after addition of 10% wheat straw biochar produced at 350 °C to 550 °C. Chintala et al. (2014) found the greatest  $q_{max}$  values (34 mmol L<sup>-1</sup>) for an acidic soil with 4% (w/w) switchgrass biochar pyrolysed at 650 °C. In a study by Rens et al. (2018), the addition of a white wood biochar pyrolysed at 450 °C to 500 °C to a sandy soil led to a 75% increase of  $q_{max}$  to 28 mg kg<sup>-1</sup>. In contrast, addition of the same biochar to a silt loam soil increased  $q_{max}$  less than 2% to 185 mg kg<sup>-1</sup>. This effect is in line with several studies that have found more pronounced effects of biochar addition to sandy soils compared to loamy soils (e.g., Gronwald et al. 2015).

Greater  $q_{max}$  values were derived in batch equilibrium experiments with pure biochars: Trazzi et al. (2016) presented a maximum PO<sub>4</sub><sup>3-</sup>-P sorption capacity  $q_{max}$  of 16.1 mg g<sup>-1</sup> for a biochar produced from miscanthus at 700 °C; Li et al. (2019) found maximum P sorption capacity of 4.8 mg g<sup>-1</sup> for a woody biochar produced at 500 °C. Takaya et al. (2016) reported maximum PO<sub>4</sub><sup>3-</sup>-P sorption capacities  $q_{max}$  between 0 and 30 mg g<sup>-1</sup> for several biochars produced from different feedstocks. The greatest  $q_{max}$  in that study was 30 mg g<sup>-1</sup>, reported for biochar made of presscake from anaerobic digestion at 600 °C to 650 °C. One of the factors that favoured this relatively very high sorption capacity is that Takaya et al. (2016) used high P concentrations of the initial batch equilibrium solutions (125 mg PL<sup>-1</sup>) with only very small amounts of biochar (0.1 g biochar per 100 mL test solution). In contrast, initial P concentrations added to the soil mixtures in our study ranged from 1.2 to 19.8 mg PL<sup>-1</sup> (Sect. 2.3), with a substrate/solution ratio of 1:5 (10 g biochar per 50 mL test solution). This observation is in line with other studies reporting improved P adsorption with increasing initial P concentrations (e.g., Chintala et al. 2014; Takaya et al. 2016; Wang et al. 2009). However, in the study by Takaya et al. (2016), the maximum amount of initially added PO<sub>4</sub><sup>3-</sup>-P that sorbed to biochar accounted for only 7%. Other batch equilibrium studies described no P sorption (e.g., Alling et al. 2014; Hollister et al. 2013; Morales et al. 2021; Palanivell et al. 2020; Soigne et al. 2014), or even P release (e.g., Yao et al. 2012; Zhang et al. 2016). Addition of 4% (w/w) rice husk char produced at 600 °C to loamy soils triggered PO<sub>4</sub><sup>3-</sup>-P release up to 72% compared to the unamended soil (Pratiwi et al. 2016). Hale et al.

(2013) reported pronounced PO<sub>4</sub><sup>3-</sup>-P release from unwashed biochars; however, after washing with millipore water, corn cob and cacao shell biochars produced in traditional kilns at 400 °C and 350 °C showed PO<sub>4</sub><sup>3-</sup>-P sorption.

In general, due to its low mobility and the ability of most soils to sorb P in the form of PO<sub>4</sub><sup>3-</sup>, P loss due to leaching is not of great concern in most soils (Sparks 2003a). Sorption of P in soils is influenced by various soil parameters, like pH, contents of iron and aluminium oxides, carbonates, organic matter, clay content, and clay mineralogy (Coulombe et al. 1996). The reddish colour and significant amounts of total Fe (2.10 g kg<sup>-1</sup>) and Al (4.91 g kg<sup>-1</sup>; see Table 1) indicate the presence of Fe- and Al-oxides in the Arenosol that might have contributed to the PO<sub>4</sub><sup>3-</sup>-P sorption of 21.7 mg kg<sup>-1</sup> ( $q_{max}$ ) of the unamended Arenosol. According to Sparks (2003b), Fe-, Al- and Mn-oxides play extremely important roles in sorption processes in soils due to their large SSA and reactivity, even if they are only present in small quantities. In our study, no further characterisation of metal oxides was conducted. We suppose that the Fe- and Al-oxides were responsible for PO<sub>4</sub><sup>3-</sup>-P sorption in the unamended Arenosol. The stepwise addition of biochar to the Arenosol led to a slight increase of  $q_{max}$ , presumably due to the addition of a certain amount of sorption sites for PO<sub>4</sub><sup>3-</sup> on the biochar. However, the effect was not linear and was more pronounced for the lowest biochar addition rates. Other than for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, SSA seems not to be an important factor in PO<sub>4</sub><sup>3-</sup> sorption (e.g., Takaya et al. 2016; Wang et al. 2015b); however, elemental composition of biochars seems to play a major role (e.g., Gronwald et al. 2015; Takaya et al. 2016; Xue et al. 2009). Several authors reported a positive correlation between PO<sub>4</sub><sup>3-</sup> adsorption and the presence of mineral salts, in particular Ca<sup>2+</sup> or Mg<sup>2+</sup>; precipitation and surface deposition on Ca<sup>2+</sup> or Mg<sup>2+</sup> present on the biochar surface are assumed to be the main mechanisms controlling PO<sub>4</sub><sup>3-</sup> sorption (e.g., Chintala et al. 2014; Pratiwi et al. 2016; Xue et al. 2009; Yao et al. 2013; Zeng et al. 2013).

Moreover, several authors assume that the increase in P sorption or precipitation after biochar addition is, due to an increase of pH, more pronounced for Ca-induced sorption and, to a lesser extent, for Fe- and Al-oxides (e.g., Eduah et al. 2019; Takaya et al. 2016; Xu et al. 2014). This assumption is in line with Schneider and Haderlein (2016), who analysed P fractions of several biochars and reported that more than two-thirds of the total P of all analysed pyrochars was inorganic Ca-bound P, whereas Fe- and Al-bound organic and inorganic P added up to less than 10%. The biochar used in this study had substantial amounts of 6.5 g kg<sup>-1</sup> Ca and 1.17 g kg<sup>-1</sup> Mg, which may be an important factor for PO<sub>4</sub><sup>3-</sup>-P sorption. Moreover, Wang et al. (2015b) found a positive linear correlation ( $R^2 = 0.73$ ) between PO<sub>4</sub><sup>3-</sup>-P sorption and the amount of base functional groups on biochar

surfaces. The contents of base functional groups and mineral salts in biochars increase with higher pyrolysis temperature (e.g., Al-Wabel et al. 2013; Cheng et al. 2018; Jung et al. 2016); this may be one possible reason for the tendency for greater  $\text{PO}_4^{3-}$  sorption rates in high-temperature biochars, as reported by several authors (e.g., Jung et al. 2016; Takaya et al. 2016; Trazzi et al. 2016; Wang et al. 2015b). In contrast, the biochar itself used in our study did not show any sorption at all, only release of  $24.5 \text{ mg PO}_4^{3-}\text{-P g}^{-1}$  (Table 4) when equilibrated for 24 h in millipore water. With a total P content of  $580.8 \text{ mg kg}^{-1}$ , the biochar used in our study had a large P reservoir; the plant-available P fraction, determined by CAL-extraction, amounted to  $71.2 \text{ mg kg}^{-1}$  (Table 1). As the water-soluble P fraction of the biochar was not removed by washing before the experiment, the equilibration released large amounts of water-soluble P that presumably exceeded the  $\text{PO}_4^{3-}$ -P sorption capacity of the biochar and evoked release of P.

#### 4.4.2 $\text{PO}_4^{3-}$ -P sorption on clay

Addition of clay stepwise increased the maximum  $\text{PO}_4^{3-}$ -P sorption capacity of the Arenosol and  $q_{max}$  of the Vertisol itself to  $176.4 \text{ mg kg}^{-1}$ . Compared with biochar, the addition of 10% clay more than doubled  $q_{max}$ . All batch equilibrium experiments relating to  $\text{PO}_4^{3-}$  sorption reviewed for our study report  $\text{PO}_4^{3-}$  sorption for numerous types of clays, e.g., Vertisols (Nunes et al. 2012; Nychas and Kosmas 1984; Solis and Torrent 1989), terra rossa (Durn et al. 2016), clayey sediments (Wang et al. 2009), clayey Cerrado soil (Barros et al. 2005), clay from crushed recycled building bricks (White et al. 2011), and clays originating from primary and secondary types of deposits (Binner et al. 2015). All the main clay minerals, such as kaolinite, illite, smectite, montmorillonite, bentonite, and saponite, are represented in these studies. Maximum  $q_{max}$  values in the studies are  $402 \text{ mg kg}^{-1}$  for a clayey river sediment (Wang et al. 2009), around  $450 \text{ mg kg}^{-1}$  for a Vertisol (Solis and Torrent 1989) and a fine calcined clay (White et al. 2011),  $1430 \text{ mg kg}^{-1}$  for terra rossa (Durn et al. 2016), and  $2566 \text{ mg kg}^{-1}$  for another Vertisol (Nunes et al. 2012). Maximum  $\text{PO}_4^{3-}$  sorption ( $q_{max}$ ) up to approx.  $3500 \text{ mg kg}^{-1}$  is reported by Binner et al. (2015) for a smectitic clay with large content of Fe oxides.

Conduction of batch experiments is a common practice to reveal sorption capacities of soils and soil components for dissolved substances such as nutrients, heavy metals, or organic compounds. However, all the above-mentioned studies derived sorption isotherms from pure clays. We only found one study, Abdelwaheb et al. (2019), which involved a batch experiment with mixtures of a sandy soil with a clayey soil. They reported a more than ninefold increase of maximum sorption capacity  $q_{max}$  of the ( $0.14 \text{ mg g}^{-1}$ ) sand

after 30% clay addition up to  $1.28 \text{ mg g}^{-1}$ . Several other studies examined the effects of clay addition to a soil in regard to  $\text{PO}_4^{3-}$  sorption or retention, but did not derive sorption isotherms. In an incubation study, Nguyen and Marschner (2013), for example, reported a significant reduction of P release after the addition of 20% (w/w) sandy clay loam to sandy soil amended with compost. Tahir and Marschner (2017) demonstrated an increase of P sorption after addition of 20% (w/w) of a clayey subsoil; while Arenosol had no P sorption capacity at all, the addition of a low smectite clay increased the maximum P sorption to  $36 \text{ mg kg}^{-1}$  and the addition of a high-smectite clay raised it to  $46 \text{ mg kg}^{-1}$ . In pot experiments, Reuter (1994) added increasing shares of two different clays to a sandy soil. The addition of 2.2% (w/w) brick clay reduced initial P leaching of around  $75 \text{ mg P}$  per pot to 0, whereas only a 0.3% (w/w) addition of bentonite was needed to achieve the same result.

Vertisols, in general, have a large sorption capacity for  $\text{PO}_4^{3-}$  (Nychas and Kosmas 1984). As mentioned in the previous section, the sorption of  $\text{PO}_4^{3-}$  is influenced by various soil parameters; in particular, P has a high affinity to sorb on mineral surfaces like clay minerals, Fe/Al oxides, and carbonates (Coulombe et al. 1996). However, even though numerous experiments have tested the  $\text{PO}_4^{3-}$  sorption ability of these single soil constituents, the relative importance of each soil parameter still remains unclear (Gérard 2016). Consequently, several studies come to contradictory explanations regarding the main factors controlling  $\text{PO}_4^{3-}$  sorption to soils. One factor controlling  $\text{PO}_4^{3-}$  sorption in soils is the large clay content that accounts for 69.8% of the Vertisol in our study (see Table 1). The dominating clay minerals are smectites, estimated 40% to 60% for this Vertisol (Mertens et al. 2017a). Smectites exhibit large SSAs ( $600 \text{ m}^2 \text{ g}^{-1}$  to  $800 \text{ m}^2 \text{ g}^{-1}$ ), have high layer charge (0.3 to 0.6 electron per half unit cell), and are rich in iron (up to 10%  $\text{Fe}_2\text{O}_3$ ) (Coulombe et al. 1996). Several authors reported a significant correlation of clay content with  $\text{PO}_4^{3-}$  sorption (e.g., Abdelwaheb et al. 2019; Barros et al. 2005; Gérard 2016; Nunes et al. 2012; Sei et al. 2002). Factors that may explain the correlation are the large SSA of clay minerals (e.g., Gérard 2016; Nunes et al. 2012; Sei et al. 2002), and their high content of structural Al and Fe (e.g., Binner et al. 2015; Sei et al. 2002). Reactive Al sites, present at the edges of clay minerals, are able to bind P through ligand exchange with hydroxyl groups (Durn et al. 2016).

Mineral surfaces form another factor of P sorption to soils. Phosphate has a relatively strong affinity to sorb on mineral surfaces (Antelo et al. 2005). A strong correlation between the presence of Al and Fe oxides and  $\text{PO}_4^{3-}$  sorption is reported by many authors (e.g., Binner et al. 2015; Gérard 2016; Nunes et al. 2012; Sei et al. 2002; Wang et al. 2012). Durn et al. (2016), for example, stated the Fe

content in clayey terra rossa to be the key controlling factor of P removal from waste water, and Solis and Torrent (1989) found a high correlation of P sorption with the Fe content of a Vertisol in short-term sorption. One explanation for the high correlation is the large SSA of Al and Fe oxides, resulting in a large number of reactive sites on the surface of the oxides (e.g., Flores-Ramírez et al. 2018; Gérard 2016; Sei et al. 2002; Wang et al. 2009). Two possible mechanisms behind  $\text{PO}_4^{3-}$  sorption to Al and Fe oxides are ligand exchange reactions and electrostatic interaction of the  $\text{PO}_4^{3-}$  anion with the charged oxide surface, where the latter is greatly controlled by the solution's pH (Antelo et al. 2005). As the Vertisol used in our study contained substantial amounts of Fe and Al (total Fe content: 6.1%; total Al content: 6.4% Table 1), we assume that Fe and Al oxides play a major role in the high sorption capacity of the Vertisol for  $\text{PO}_4^{3-}$ .

Under neutral and alkaline conditions, Vertisols also contain significant amounts of carbonates (Coulombe et al. 1996). No carbonate analysis was conducted in our study; however, the rather large total Ca content of 3.8% in combination with the slightly alkaline pH of 8.3 ( $\text{H}_2\text{O}$ ) indicates the presence of substantial carbonate supplies in the Vertisol. Low but significant correlation between the carbonate content of clayey material and  $\text{PO}_4^{3-}$  sorption is reported in several studies (e.g., Nunes et al. 2012; Wang et al. 2009), especially for long-term sorption up to 144 days after P addition (Solis and Torrent 1989). However, a significant share of  $\text{PO}_4^{3-}$  sorption to carbonates may take place as co-precipitation of Ca-phosphates with low solubility, contributing to  $\text{PO}_4^{3-}$  fixation in soils (e.g., Coulombe et al. 1996; Wang et al. 2009). Even though several authors claimed organic matter plays a role in P sorption, (e.g., Nychas and Kosmas 1984; Sparks 2003a; Wang et al. 2009), the low total C content of only 1.7% (Table 1) may not play a significant role for P sorption in this study. Nunes et al. (2012) found only a low and not significant correlation of organic matter to  $\text{PO}_4^{3-}$  sorption of a Vertisol but acknowledged the relevance of organic carbon for  $\text{PO}_4^{3-}$  sorption for other soil types. In conclusion, we assume that the P sorption to the Vertisol in this study is mainly controlled by sorption to clay minerals, in particular to smectites, Fe/Al oxides, and, to a lesser extent, carbonates that may form low-soluble Ca-phosphates.

## 5 Conclusions

The biochar and clay tested in this study both indicated the potential to increase the nutrient sorption capacity of a tropical Arenosol, even when added in small amounts. For biochar, batch equilibrium experiments demonstrated a marginal increase of  $\text{PO}_4^{3-}$ -P and  $\text{NH}_4^+$ -N sorption capacity,

a slight reduction of  $\text{NO}_3^-$ -N release from the Arenosol, and massive release of  $\text{K}^+$  from the biochar. Biochar itself was also subject to  $\text{PO}_4^{3-}$ -P release. Clay, in contrast, showed better efficacy in increasing the sorption capacities of  $\text{NH}_4^+$ -N,  $\text{K}^+$ , and  $\text{PO}_4^{3-}$ -P but had no effect on  $\text{NO}_3^-$ -N sorption capacity.

Moreover, biochar exhibits the potential to augment soil fertility by adding nutrients to soils, in particular K, and may act as a slow-release fertiliser over a prolonged time span. To ensure a greater stability of biochars in soils, we recommend pyrolysis temperatures above 600 °C. We also recommend using locally abundant biomass from sustainable sources to avoid conflicts with food production for biochar carbonisation. Before adding large quantities to soils, biochars should be tested for contaminants such as polycyclic aromatic hydrocarbons, dioxins, furans, and heavy metals that may be released from the biochar into the soil (Qadeer et al. 2017).

Clays are more resistant to degradation than biochars and may perpetuate their soil-amending properties for a long time. We recommend substrates with large clay content and preferably smectitic mineralogy, which show high potential to increase nutrient sorption and water-holding capacity. Clayey material should come from locally available and sustainable sources, for example, clay-rich subsoils or natural clay deposits. As in the present study, clayey sediments from water bodies can also be used as to meliorate soils. However, a screening for toxic substances should be conducted before large scale field application to avoid contamination of the amended soil.

To combine the positive soil-amending effects of both materials, we suggest mixing biochar and clay. Clay may help stabilise the organic material and may adsorb the K released from the biochar, whereas the biochar may retain highly mobile  $\text{NO}_3^-$ -N. However, further research is needed to assess the soil-amending potential of biochar–clay mixtures.

In conclusion, we recommend a careful selection of soil conditioners according to their properties to complement the soil. Before field application, the suitability of the soil conditioner should be tested in preliminary analyses, for example, batch equilibrium experiments. The high costs and efforts required to incorporate biochar or clay should also be considered. To evaluate the long-term efficacy of the effects of biochar and clay on sorption capacity of soils, further investigations are needed, particularly under realistic conditions at the field scale.

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**Authors' contributions** CB: writing of manuscript, provisioning of field samples, design and conduction of experiment, literature research, data analysis, discussion, revision of text. DM: design and conduction of experiment, literature research, discussion, revision of text. AC: support of data analysis, discussion, revision of text. MK: supervision of experiment, discussion, revision of text. The authors read and approved the final manuscript.

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**Availability of data and materials** The data and material used in this study will be made available by the authors upon request.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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