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Biochar increases plant available water in a sandy soil under an aerobic rice cropping system

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SED

6, 887–917, 2014

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Abstract

The main objective of this study was to assess the impact of biochar rate (0, 8, 16 and 32 t ha^{-1}) on the water retention capacity (WRC) of a sandy Dystric Plinthosol. The applied biochar was a by-product of slow pyrolysis ($\sim 450\,°$C) of eucalyptus wood, milled
5   to pass through a 2000 µm sieve that resulted in a material with an intrinsic porosity ≤ 10 µm and a specific surface area of ~ 3.2 m^2 g^{-1}. The biochar was incorporated into the top 15 cm of the soil under an aerobic rice system. Our study focused on both the effects on WRC and rice yields at 2 and 3 years after application. Undisturbed soil samples were collected from 16 plots in two soil layers (5–10 and 15–20 cm). Soil wa-
10 ter retention curves were modelled using a nonlinear mixed model which appropriately accounts for uncertainties inherent of spatial variability and repeated measurements taken within a specific soil sample. We found an increase in plant available water in the upper soil layer proportional to the rate of biochar, with about 0.8 % for each t ha^{-1} of biochar amendment at 2 and 3 years after application. The impact of biochar on soil
15 WRC was most likely related to an increase in overall porosity of the sandy soil, which was evident from an increase in saturated soil moisture and macro porosity with 0.5 % and 1.6 % for each t ha^{-1} of biochar applied, respectively. The increment in soil WRC did not translate into an increase in rice yield, essentially because in both seasons the amount of rainfall during critical period for rice production exceeded 650 mm. The use
20 of biochar as a soil amendment can be a worthy strategy to guarantee yield stability under water limited conditions. Our findings raise the importance of assessing the feasibility of very high application rates of biochar and the inclusion of a detailed analysis of its physical and chemical properties as part of future investigations.

1 Introduction

Soil water retention capacity (WRC) is a potential indicator of soil quality and productivity. Several agronomic practices such as no-tillage, mulching and cover crops are implemented aiming to improve soil physical properties. An enhanced soil WRC through the adoption of these practices is attained via protection of the soil surface, improved soil aeration and infiltration, or an increased soil organic matter level. The use of carbonised biomass, or biochar, has been regarded as an interesting option for improving soil physical properties (Glaser et al., 2002). The rising demand for charcoal by iron smelters in Brazil has resulted in a rapid increase in the area covered with timber plantations. Between 2005 and 2010 the total increase was 23 %. In 2010, forest plantations in Brazil covered six million hectares of which 73 % comprised of eucalyptus forests. Of all produced wood, around 35 % was destined to charcoal production (ABRAF, 2010). Small pieces of char (< 8 mm) have to be compacted into bricks if they are to be used as charcoal by iron smelters. Alternatively, these pieces can be recycled as soil amendment. Potentially, a large quantity of this type of biochar is available for Brazilian farmers. It is this material that was tested in the current study.

Tryon (1948) showed that soil moisture at field capacity in a sandy soil increased linearly with increasing wood biochar application rate. Several recent studies have also reported the potential of wood biochar to increase WRC of sandy soils (Pereira et al., 2012; Dempster et al., 2012; Basso et al., 2013; Abel et al., 2013; Ibrahim et al., 2013). The majority of studies were conducted under artificially controlled conditions, testing the effect of a wide range of biochar amounts on WRC. Though such studies are useful, the extrapolation of their results to field conditions present some limitations: (i) the amounts of biochar tested are often larger than what is practically and economically feasible for incorporation into agricultural fields; (ii) the conditions for biochar application in artificially packed soil samples might lead to artefacts not normally encountered under field conditions, where biochar is incorporated via tillage and crops are grown afterwards; and (iii) the consolidation time is usually shorter in artificially controlled

conditions than under field trials. Thus, more long term studies on the effect of biochar under field conditions are required.

The increment in available water following biochar application is commonly related to the porous structure of the material. The pores behave as additional capillaries, favour-
5   ing the WRC of the soil. Primarily, the number and size of pores is determined by the type of feedstock, temperature level and time of pyrolysis. The specific surface area (SSA) of biochar increases with temperature of pyrolysis (Lei and Zhang, 2013; Borne-mann et al., 2007). At temperatures of 450 °C the SSA can be smaller than $10\,\mathrm{m^2\,g^{-1}}$, while at temperatures of 600–750 °C it can rise to around $400\,\mathrm{m^2\,g^{-1}}$ (Kookana et al.,
10 2011). Clearly, SSA is a characteristic that should be considered when the impact of biochar on soil WRC is investigated. Secondly, the particle size of biochar can be a de-terminant of the potential positive effect on soil WRC. Tryon (1948) showed that the impact on soil WRC was higher with finer material ($< 1000\,\mu m$) than with larger particle sized biochar (2000–$5000\,\mu m$).
15 The soil WRC is represented by the nonlinear relation between volumetric soil moisture and matric potential, referred to as the soil water retention curve (SWRC). Such curves can be used as indicators of changes in soil physical properties caused by the incorporation of biochar into the soil matrix. The van Genuchten model (van Genuchten, 1980) is one of the most widely used representations of the soil WRC. Gen-
20 erally, statistical programs specifically designed to fit SWRC only allow fitting of curves for isolated treatments, without accounting for experimental structure (e.g., Dourado-Neto et al., 2000). The isolated treatment-specific model fitting has three main disad-vantages: (i) comparison of SWRC between treatments via formal statistical tests is not possible due to the absence of an error structure that accounts for overall vari-
25 ance within treatments; (ii) autocorrelations among random errors of moisture mea-surements taken in the same sample unit (the cylinder) under different matric poten-tials are ignored, leading to incorrect quantification of model uncertainty; and (iii) the spatial variability, likely to be high under field conditions, cannot be fully accounted for

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(Omuto et al., 2006). In this study we propose the use of nonlinear mixed (NLM) model to overcome these disadvantages.

Circa 40 % of overall Brazilian crop production is located in the Brazilian Midwest region (IBGE, 2012), where our study was conducted. The predominant biome in this region is a tropical savannah. Though a tropical savannah is a drought prone environ-ment (Peel et al., 2007), Brazilian farmers usually manage to grow two crops during the wet season (from October to March). However, rising temperatures and changes in rainfall distribution pattern have decreased the chances of an economically successful second harvest. Further temperature rises are projected to provoke decreases in suit-able area for cultivation of the majority of crops in Brazil, mainly due to an increase in evapotranspiration (Assad et al., 2008). This further stresses the need of agronomic measures able to increase the water use efficiency in crop production.

The current study is a continuation of the experiment described by Petter et al. (2012), in which they showed that rice yields increased with around $3\,\%\,\mathrm{t\,ha^{-1}}$ biochar amendment in the first and second seasons after application. Additionally, in a pot experiment using a sterile sand, Pereira et al. (2012) observed an increase in soil WRC at matric potentials lower than $-6\,\mathrm{kPa}$ with a rate of 12 % w/w of a similar biochar as the one tested in this study, accompanied by a delay in the point where rice transpiration rate is affected by water stress and declines. Hence, the main objective of this study was to test the impact of a range of wood biochar rates (up to 1.5 % w/w) on both soil WRC and rice yields on a sandy Dystric Plinthosol at 2 and 3 years after application under field conditions. As part of this endeavour, we present the novel use of a nonlinear mixed (NLM) model for estimating shape parameters of the SWRCs.

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2   Material and methods

2.1   Experimental set up and biochar characterization

In 2008, a permanent non irrigated field trial was set up at Estrela do Sul Farm in Nova Xavantina, Mato Grosso, in the Brazilian Midwest region on sandy Dystric Plinthosol
[5] (76 % sand, 17 % clay). The Köpper–Geiger climate classification of the region is Aw (Peel et al., 2007). The monthly precipitation and average temperatures since the start of the field trial is presented in Fig. 1, based on data from Agritempo (2014). Details on the history of the field trial and soil chemical properties can be found in Petter et al. (2012), who reported on the influence of biochar application on rice growth and
[10] yields at one month and at one year after application. Here we report on the most recent growing seasons of rice: from 13 December 2010 to 2 April 2011, and from 13 December 2011 to 2 April 2012, corresponding to two (S2) and three (S3) years after biochar application, respectively. Our analysis focuses on the influence of biochar on two variables, namely soil WRC and rice yields. Biochar was applied once, when the
[15] field trial was established on 5 December 2008. Four levels of mineral fertilisation were applied in strips, and the four levels of biochar (0, 8, 16 and 32 t ha^{-1}) where applied within the strips in a randomized block design, with four replicates. Sixteen treatments were used, resulting in a total of 64 experimental plots, each with an area of 40 m^2 (4 × 10 m). Mineral fertilisation was always applied in strips across the four blocks. In
[20] S2 and S3, four levels of N-fertilisation (0, 30, 60 and 90 kg N ha^{-1}) were applied and all plots were given the same rate of P-K (kg ha^{-1}) at sowing (60–20 in S2, and 30–30 in S3) taking into account the soil chemical analysis prior sowing and fertilise recommendations for aerobic rice systems in the Brazilian savannah (EMBRAPA, 2007). The N-fertiliser (urea) was divided into three applications: at sowing and at 25 and 45
[25] days after emergence (DAE). Rice (BRS Primavera) was sown directly with a 5-row Semeato® planter adapted for no-tillage systems, with space between rows of 45 cm and 110 seeds m^{-1}. Weeds infestation was chemically controlled with Glyphosate®

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($5 \, \text{L ha}^{-1}$) applied at around 15 days prior to sowing and with 2–4 D ($0.7 \, \text{L ha}^{-1}$) or Star Rice® ($0.4 \, \text{L ha}^{-1}$) around 10 DAE. Additionally, manual weeding operations were conducted at around 45 and 75 DAE.

Air dried biochar (particle size $\leq 2000 \, \mu\text{m}$) was spread manually on the soil surface, and incorporated into the upper 15 cm, using a harrow. The amount of biochar applied to the upper 15 cm was based on the average amount of pyrogenic C found in the fertile anthropogenic dark earths (ADE) of the Amazon. According to Glaser et al. (2001) the upper 30 cm of the ADE soils contain around $25 \, \text{t ha}^{-1}$ pyrogenic C, corresponding to an amount of $12.5 \, \text{t ha}^{-1}$ within 0–15 cm soil layer. As the biochar tested in our field trial had a concentration of 77 % pyrogenic C, we applied a lower ($8 \, \text{t ha}^{-1}$), similar ($16 \, \text{t ha}^{-1}$) and higher ($32 \, \text{t ha}^{-1}$) rate of biochar than the amount of pyrogenic C found in ADE. Considering the soil bulk density and depth where biochar was applied, the application rate on a dry mass basis (weight of biochar/total weight of soil), was equivalent to 0.4, 0.7, and 1.5 % w/w. The biochar was made of eucalyptus timber via slow pyrolysis in a cylindrical metal kiln using temperatures around 400–500 °C. A single point surface area of biochar was determined by the Brunauer, Emmelet and Teller (BET) nitrogen absorption method (Brunauer et al., 1938), using nitrogen gas sorption analysis at 77.3 K (-195.9 °C). The specific surface area (SSA) of the biochar applied, with a bulk density of $0.3 \, \text{g cm}^{-3}$, was $3.2 \pm 0.5 \, \text{m}^2 \, \text{g}^{-1}$. The porous structure of the biochar (pore size $\leq 10 \, \mu\text{m}$) is shown in Fig. 2. Chemical properties of biochar were described in Petter et al. (2012).

2.2 Measurements on soil WRC and the modelling of SWRCs

The soil WRC was evaluated at two (S2) and three (S3) years after biochar application. Soil samples (cylinders of inox steel of 5 cm height and 5 cm diameter) were collected from mini-trenches 50 cm deep between rows of rice around 75 DAE. Setting of mini-trenches was completely randomized among two strips located at the right and left borders of the field trial (2 replicates for each biochar rate within each strip). Since the

biochar was incorporated into the upper 15 cm layer, soil samples were collected in the centre (5–10 cm) and just below (15–20 cm) this layer to account for an effect of biochar that had possibly moved out the original layer. Samples were collected from 16 plots (4 biochar rates × 4 plots, one sample per soil layer per plot) in a moist soil

5 on 15 March 2011 and on 3 March 2012. The soil WRC was determined according to EMBRAPA (1997). Samples were saturated with water for 12 h and analysed in a centrifuge Kokusan H-1400pF®, four samples at a time, for 30 min under seven speed levels: 600, 700, 800, 1300, 1800, 2400 and 9100 rpm (equivalent to 0, 33.00, 44.92, 58.67, 154.93, 297.03 and 528.05 g). The volume of the soil water in the samples sub-

10 jected to different speeds corresponded to seven matric potentials: −6, −8, −10, −33, −60, −100 and −1500 kPa. The bulk density was determined as the ratio between the dried mass of soil and the volume of a cylinder. The bulk density was used to calculate the volumetric soil moisture ($cm^3 cm^{-3}$). Saturated soil moisture was determined as the soil moisture content in saturated samples at 0 kPa right before subjecting samples to

15 different speeds in the centrifuge.

The relation between observed volumetric soil moisture and soil matric potential (the soil water retention curve – SWRC) was determined by fitting the van Genuchten model described in Eq. (1).

$$\theta(\psi) = \theta_r + (\theta_s - \theta_r) \left[\frac{1}{1 + (\alpha\psi)^n} \right]^m \tag{1}$$

20

where, $\theta(\Psi)$ is the volumetric soil moisture ($cm^3 cm^{-3}$) at a given matric potential Ψ (kPa); θ_r is the residual soil moisture (soil moisture content at a $\Psi \geq -1500$ kPa); θ_s is the saturated soil moisture (soil moisture content at 0 kPa); and m, α, and n are shape parameters. The Mualen constraint $m = 1 - 1/n$ (Mualem, 1976) was adopted

25 to increase model parsimony.

We used a nonlinear mixed (NLM) model for uncertainty assessment of SWRC estimates by considering the whole experimental design structure to quantify residual variance. For parsimony and to reduce the risk of non-convergence, we have set θ_r

and θ_s as known parameters. By adopting such approach, the uncertainty of the estimates of shape parameters α and n and the test of the null hypothesis of interest were performed considering the overall variance of soil moisture arising from within treatments variance. Further, the NLM model permits accounting for potential random
5 effects associated to plot location, as proposed by Omuto et al. (2006). In our study, correlations among measurements taken within the same sample unit (one cylinder per plot for each soil depth) were accounted for by including plot as a random effect u in the model. The core of the NLM model adopted is the van Genuchten–Mualen model (Eq. 1). The generic NLM model used to estimate the SWRC for each biochar level
10 within two soil layers and two years was given by Eq. (2):

$$\hat{\theta}_{ijk} = \theta_{r(ij)} + (\theta_{s(ij)} - \theta_{r(ij)}) \left[\frac{1}{1 + (\alpha_i \psi_{ijk})^{n_i}} \right]^{1-1/n_i} + e_{ijk} + u_l \qquad (2)$$

where $\hat{\theta}_{ijk}$ is the predicted soil moisture of the treatment level i ($i = 0, 8, 16, 32\,\text{t}\,\text{ha}^{-1}$) in the replication j ($j = 1, 2, 3, 4$) at a matric potential k ($k = -6, -8, -10, -33, -60$,
15 $-100\,\text{kPa}$); $\theta_{r(ij)}$ and $\theta_{s(ij)}$ are the measured soil moisture at treatment level i in replicate j at $-1500\,\text{kPa}$ and $0\,\text{kPa}$, respectively; α_i and n_i are the shape parameters for each treatment level i; $e_{ijk} \sim N\,(0, \sigma^2)$, is the random error associated to each measurement $\hat{\theta}_{ijk}$; and $u_l \sim N\,(0, \Sigma)$, represents the random effect of latent variables associated to location of a plot l ($l = 1, \ldots, 16$).
20   The residual soil moisture ($\theta_{r(ij)}$) was assumed as the measured soil moisture content at $-1500\,\text{kPa}$ and the saturated soil moisture ($\theta_{s(ij)}$) as the measured soil moisture content at $0\,\text{kPa}$. Shape parameters were estimated using the maximum likelihood method, implemented in NLMIXED Procedure of the SAS/STAT® software (SAS Institute Inc., 2008). Comparisons of shape parameters between treatments control and
25 biochar were performed by t tests for linear contrasts.

2.3 Analysis of soil physical-hydric variables response to biochar rate

The response of some key soil physical-hydric variables to biochar rate was evaluated via measurements of: (i) soil bulk density (BD); (ii) saturated soil moisture (θ_s); (iii) residual soil moisture (θ_r); (iv) macro porosity (MAC), as the predicted soil moisture content between 0 and -6 kPa ($\hat{\theta}_0 - \hat{\theta}_6$); (v) rice available water (RAW), as the predicted soil moisture content between -6 and -100 kPa ($\hat{\theta}_6 - \hat{\theta}_{100}$); and (vi) plant available water (PAW) as the predicted soil moisture content between -6 and -1500 kPa ($\hat{\theta}_6 - \hat{\theta}_{1500}$). The predicted volumetric soil moisture ($\hat{\theta}$) was estimated via model described in Eq. (2). The RAW was also estimated considering that the critical soil water volume for rice production should be defined at a matric potential of -100 kPa according to Wopereis et al. (1996).

Response of physical-hydric soil variables to biochar rate were analysed for each year and soil layer separately via the quadratic model described in Eq. (3):

$$y_{ij} = \beta_0 + \beta_1 \text{char}_i + \beta_2 \text{char}_i^2 + e_{ij} \tag{3}$$

where, y_{ij} is the observation of the response variable y corresponding to biochar level i ($i = 0, 8, 16, 32 \text{ t ha}^{-1}$) of the replication j ($j = 1, 2, 3, 4$); β_0 is the intercept; β_1 and β_2 are the linear and quadratic effects of biochar, respectively; and e_{ij} is the random error associated to each observation y_{ij}.

Analyses were performed using the MIXED procedure (Proc MIXED) of the statistical software SAS/STAT® (SAS Institute Inc., 2008). The magnitude of the biochar effect was assessed by nominal significance levels (p values) derived from hypothesis testing of β_1 and β_2 estimates. Due to the large experimental area, relatively high residual variances were anticipated to occur. For that reason, we adopted 0.10 as the appropriate p value for the selection of model predictors in order to safeguard against high type II error.

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2.4 Measurement and analysis of rice yield and yield components

The response of rice yield and yield components was measured for all biochar and N-fertilisation treatments. At crop maturity, around 100 DAE, total shoot dry matter, grain yield (weight of rice grains dried to 13 % moisture) and yield components (number of
5   panicles, grains panicle^{-1}, grain filling index and 1000-grain weight) were determined in samples collected from 2 rows of 3 m in the centre of each plot. Harvest index was calculated as the ratio between grain yield and total shoot dry matter. Filled and unfilled grains from panicles within the harvested area were separated with a vertical blower and counted with a seed counter. Grain filling index was calculated as the ratio between
10   the number of filled grains and the total number of grains.

    We used a linear mixed model instead of the commonly used design based ANOVA to analyse the data due the incomplete randomisation of N treatments. The linear mixed model adopted allowed us to account for potential spatial auto-correlation among plot measurements. Location of a plot was established by its position in a specific block and
15   row within a block. The location of a plot was included as a random effect. Biochar, N, biochar × N and quadratic terms were included as fixed effects. Model parameters were estimated by the restricted maximum likelihood method – REML. Analyses were performed using the Mixed Procedure (Proc MIXED) of the statistical software SAS/STAT$^{\circledR}$ (SAS Institute Inc., 2008). Graphical residual analysis, influence diagnostics and check-
20   ing for potential violation of model assumption were conducted using the ODS GRAPH-ICS option. Response surfaces for identifying patterns of response of rice yields and yield components to biochar and N treatments were modelled for each season separately. A complete quadratic model (Eq. 4) in which all predictors (biochar, N and biochar × N) were included was the starting point:

25   $$y_{ijbr} = \beta_0 + \beta_1 \text{char}_i + \beta_2 \text{N}_j + \beta_3 \text{char}_i \cdot \text{N}_j + \beta_4 \text{char}_i^2 + \beta_5 \text{N}_j^2 + c_b + d_r + e_{ijbr} \qquad (4)$$

where y_{ijkl} is the observation of the response variable y corresponding to biochar and N treatments i ($i = 1, 2, 3, 4, \ldots, 16$) of the replication j ($j = 1, 2, 3, 4$); β_0 is the inter-

cept; β_1 and β_2 are linear effects of biochar and N, respectively; β_3 is the interaction effect biochar $\times$ N; β_4 and β_5 are quadratic effects of biochar and N, respectively; c_b and $d_r \sim N (0, \Sigma)$ are the potential random effects related to location of a plot in a block b ($b = 1, 2, 3, 4$) and in a row r ($r = 1, 2, 3, 4$) within a block b; and $e_{ijbr} \sim N (0, \sigma^2)$ is the random error associated to each observation y_{ijbr}.

Again, we adopted 0.10 as the appropriate p level in the process of predictors' selection. To determine the appropriate response surface, predictors containing the highest p value ($p > 0.10$) were progressively excluded respecting the hierarchy of effects: linear terms were retained whenever interaction or quadratic terms were significant (MacCullagh and Nelder, 1983). The magnitude and evidence of the effects was assessed by estimates and their respective nominal significance levels.

3 Results

3.1 The use of NLM to adjust SWRCs and effects of biochar rate on shape parameters

Overall, the goodness of fit was high (R^2: 0.77 to 0.98), indicating the adequacy of the proposed nonlinear mixed (NLM) model to estimate the shape parameters of the SWRCs (Table 1). Inclusion of the random effect u significantly increased the accuracy of the SWRC modelling (Fig. 3). The consistent SWRC underestimation at high matric potential was likely due to increases in soil moisture content with biochar application, which was particularly evident from SWRCs for treatments with 8 and $32\,\text{t}\,\text{ha}^{-1}$ in the upper and lower soil layers in S2.

The evidence of the effects of biochar on shape parameters can be seen through changes in patterns of the SWRCs. At 2 years after biochar application in both soil layers for the treatment with $8\,\text{t}\,\text{ha}^{-1}$ the shape parameters α and n were significantly lower and higher than control, respectively (Table 1). Also in S2, in the upper layer 5–10 cm, for the treatment with $32\,\text{t}\,\text{ha}^{-1}$ the parameter α was lower ($p \leq 0.10$) than

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the control. The SWRCs in the upper layer for the treatment with 8 and 32 t ha^{-1} were above that of the control treatment at matric potentials between −0.03 kPa and −33 kPa (Fig. 4). In S2, the most significant difference ($p \leq 0.05$) was for the parameter n of the treatment with 8 t ha^{-1} in the lower soil layer 15–20 cm. The SWRC in the lower layer for the treatment with 8 t ha^{-1} was above that of control at matric potentials between −1 and −10 kPa.

In S3, no significant effects of biochar amendment on shape parameters were observed. In the upper layer, the SWRCs of the treatments with biochar amendment were all above the SWRC of the control treatment at matric potentials higher than −1 kPa, whereas at matric potentials lower than −10 kPa, the soil moisture content dropped abruptly to below that of the control treatment. This was particularly evident with 32 t ha^{-1}. In S3, in the lower soil layer, the same pattern was observed, but in this layer soil moisture content for treatments with biochar dropped under matric potential lower than −6 kPa, except for the SWRC of the highest biochar treatment (32 t ha^{-1}), which was now slightly below that of the control treatment already under matric potential higher than −1 kPa.

3.2 Response of soil physical-hydric variables to biochar application rate

Most significant responses to biochar application rate were observed in the upper soil layer (5–10 cm), with minor responses in the lower soil layer (15–20 cm; Table 2). In the upper layer, RAW and PAW increased linearly with biochar application rate. The increment in RAW and PAW was with around 1 and 0.8 % for each t ha^{-1} of biochar applied or 21 and 17 % with 1 % w/w rate of biochar amendment, respectively. The response of RAW and PAW to biochar rate was stronger in S3 ($p \leq 0.05$) than in S2 ($p \leq 0.10$), with narrower confidence intervals in S3 (Fig. 5).

In S2 in the lower layer only BD was significantly affected by biochar application. The response of BD (mean ± standard error) to biochar rate followed a quadratic trend, with maximum at 16 t ha^{-1} (1.684 ± 0.013) and a minimum at control (1.639 ± 0.015). In S3,

in the upper layer, saturated soil moisture (θ_s) and MAC increased linearly ($p \leq 0.05$) with 0.5 and 1.6 % for each t ha^{-1} of biochar applied, respectively; whereas in the lower layer only MAC was significantly affected by biochar application. The response of MAC to biochar rate in the lower layer followed a quadratic pattern with maximum at 16 t ha^{-1}

5 (0.2299 ± 0.0152) and minimum at 32 t ha^{-1} (0.1744 ± 0.0184).

3.3 Response of rice yields and yield components to biochar and N application rate

There was no response of rice yields to biochar application rate in either season (Table 3). In S2, total shoot dry matter (TDM) and grain yield (GY) were not affected

10 by biochar or N application rate. Both TDM and GY varied greatly, from 0.57 and 0.17 t ha^{-1} (with 32 t ha^{-1} and without N) to 4.04 and 1.99 t ha^{-1} (with 32 t ha^{-1} and 90 kg N ha^{-1}), respectively. Most significant ($p \leq 0.05$) effects of biochar were observed on number of grains panicle^{-1} (GP) and grain filling index (GFI). The response of GP and GFI to biochar rate followed a quadratic pattern with a minimum obtained at about

15 16 t ha^{-1}. The response of harvest index (HI) and number of panicles m^{-2} (PAN) to N rate followed a quadratic pattern with a maximum at around 30 to 60 kg N ha^{-1}. The estimated HI (mean ± standard error) varied from a minimum at 0.42 ± 0.02 (with 90 kg N ha^{-1}) to a maximum at 0.53 ± 0.02 (with 30 kg N ha^{-1}) and PAN from 109 ± 7 (without N) to 133 ± 5 (with 60 kg N ha^{-1}). The GFI and 1000-grain weight (GW) de-

20 creased with increasing N rate.

A year later, in S3, the effect of biochar on any characteristic measured at crop maturity of rice was totally absent. The response of TDM and PAN to N rate followed a quadratic pattern with a maximum at 30 to 60 kg N ha^{-1}, whereas GY and GFI increased linearly with increasing N rate. Estimated GY increased from 0.49 ± 0.2 t ha^{-1}

25 (without N) to 0.69 ± 0.2 t ha^{-1} (90 kg N ha^{-1}), regardless of biochar application (Table 3). The observed GY varied from 0.38 (with 8 t ha^{-1} and without N) to 0.93 t ha^{-1} (with 16 t ha^{-1} and 60 kg N ha^{-1}). The HI and GP were not affected by N treatments, whereas GW decreased linearly ($p \leq 0.10$) with increasing N rate. The GY in both

seasons were rather low, mainly due to weeds infestation. Chemical and mechanical controls were applied when necessary, but these could not sufficiently compensate for the low resistance of the cultivar BRS Primavera to biotic stresses.

4   Discussion

Here we summarize and discuss the main findings of this study as follows: (i) the impact of the wood biochar application rate on WRC of the sandy Dystric Plinthosol is positive and persistent at 2 and 3 years after application; (ii) although soil WRC increases with biochar application rate, we did not observe any impact on rice yield; and (iii) the proposed nonlinear mixed (NLM) model was an innovative analytical tool for such a large field trial.

Our results showed that in both seasons PAW and RAW in the upper 5–10 cm layer of the sandy soil increased proportionally to biochar application rate with about 0.8 and 1 % for each $t\,ha^{-1}$ of biochar applied, respectively (Fig. 5). The consistent increase in soil WRC seems to be related to a slight increase in soil moisture at $-6\,kPa$ for the treatment with $32\,t\,ha^{-1}$, as can be observed by means of SWRCs in S2 and S3 (Fig. 4), with a significant effect on the shape parameter α in S2 (Table 1). In S2 we also observed significant changes in shape parameters of the SWRC with $8\,t\,ha^{-1}$ (Table 1). However, there was no such effect for the treatment with $16\,t\,ha^{-1}$, where the increase in soil WRC seems to be a consequence of a decrease in soil moisture content with biochar rate up to $16\,t\,ha^{-1}$ at matric potentials of $-100\,kPa$ ($p \leq 0.13$) and $-1500\,kPa$ ($p \leq 0.16$) in S2. The uncertainty of the linear response of PAW and RAW to biochar rate was higher in S2 than in S3, predominantly for rates of 8 and $16\,t\,ha^{-1}$ (Fig. 5). The uncertainty can be related to changes in BD affecting the overall response to biochar application. In fact, BD was generally 1.7 % higher in S2 than in S3 (Table 2), which was a consequence of mechanical weeding using a tractor which passed twice over all plots of the field trial just prior to sowing in S2. Even though we observed no effect of

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biochar rate on BD in the upper soil layer, in the lower soil layer 15–20 cm BD increased with biochar rate up to 16 t ha^{-1}.

At matric potentials lower than −8 kPa the amount of water in soils treated with biochar decreased abruptly in both years while in S3 in the upper soil layer θ_s and MAC increased significantly with increasing biochar rate (Table 2). It seems that biochar application lead to an increase in soil moisture at a matric potential up to around −6 and −8 kPa that was not necessarily sustained under lower matric potentials (Fig. 4). Therefore, the effect of biochar on soil WRC is most likely a consequence of an increase in overall porosity of the soil. We found a notable increase in MAC of 51 % with 1.5 % w/w biochar amendment. The increase in MAC with biochar application rate was mostly related to the large particle size ($\leq$ 2000 μm) of the biochar tested. For instance, Abel et al. (2013) reported an increase of 15 % in total porosity and 6 % in air capacity with application of 5 % w/w beech wood biochar (particle sized < 5000 μm) that lead to a 35 % increase in PAW in a loamy sand soil. According to the van Genuchten model described by Ibrahim et al. (2013), there was an 8 % increase in PAW with application of 1.5 % w/w very fine particle sized biochar (44–149 μm) in a sandy loam soil. Additionally, the SWRCs that they modelled indicate a greater impact on soil WRC at low matric potentials. However, application of fine particle size material under field conditions is difficult since it is easily moved by wind. Combination of biochar with liquid or solid fertilisers could be an option to avoid such kind of losses and capture the potential positive effect of biochar on soil WRC. Liu et al. (2012), for example, observed that application of 20 t ha^{-1} of biochar with 50 t ha^{-1} of organic compost has a more prominent positive effect on water availability than application of pure compost.

The biochar we applied in the field trial is a by-product of slow pyrolysis (under ∼ 450 °C) of eucalyptus wood, which resulted in a material with an intrinsic porosity $\leq$ 10 μm (Fig. 2) and a relatively much lower SSA (3.2 m^2 g^{-1}) if compared to a wood biochar produced under greater temperature of pyrolysis, such as the one tested by Dempster et al. (2012). They observed an astonishing increment in volumetric soil moisture content at very low matric potentials of −100 and −1500 Kpa by 71 and

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127 %, respectively, with application of 1.8 % w/w biochar (SSA 273 $m^2 g^{-1}$) artificially packed with a sandy soil. Logically a higher SSA biochar has more and finer pores and therefore a greater effect on soil WRC, as demonstrated by Lei and Zhang (2013). They observed a tremendous increase in soil water content between −33 and −1500 kPa in

5   a sandy loam soil treated with 5 % w/w woodchip biochar pyrolysized at 300, 500 and 700 °C (SSA 24, 67 and 124 $m^2 g^{-1}$) of 39, 51 and 55 %, respectively. We found a rise of 6, 13 and 26 % in PAW, accompanied by a 4, 8 and 16 % increase in θ_s with 0.4, 0.7, and 1.5 % w/w biochar, respectively (Table 2). Relatively, the increase in θ_s is much higher than the 0.2 % increase with 1 % w/w biochar observed by Abel et al. (2013).

10 The rise in PAW that we found, though, is lower than the 28 % rise observed by Abel et al. (2013), and higher than the 6 % rise found by Ibrahim et al. (2013) with 1 % w/w biochar. Apart from differences in time after application and conditions of experimental setup, SSA of the biochar used is probably the main cause for these discrepancies. However, neither Abel et al. (2013) nor Ibrahim et al. (2013) determined the SSA of the

15 biochar they used. High resolution images indicate that there are differences in the pore structure of the beech wood biochar used by Abel et al. (2013) and the one used in our study (Fig. 2). The SSA of the biochar we used is similar to the birch wood biochar (particle sized < 10 000 µm) used by Karhu et al. (2011) but lower than the SSA of the eucalyptus biochar produced at 450 °C (milled to powder) described by Borneman

20 et al. (2007). Karhu et al. (2011) observed an effect in gravimetric soil moisture at 0 kPa relatively higher than the effect we observed on volumetric soil moisture at 0 kPa (θ_s) with application of 0.3 % w/w biochar.

Beyond the influence that both SSA and particle size of biochar have per se on the soil WRC of a sandy soil, we must also consider the application rate. The maximum

25 rate applied in our study was of 1.5 % w/w, which is half of the minimum rate (3 % w/w) used in other studies that have shown great impact of biochar on soil WRC of sandy soils in artificially controlled conditions (Tryon, 1948; Pereira et al., 2012; Basso et al., 2013). For instance, Basso et al. (2013) found a spectacular increase in available water content between −10 and −1500 kPa of 44 and 38 % with application of 3 and

6 % *w/w* fast pyrolysis red oak biochar, respectively. Feasibility of application of such high rates in agricultural fields should be assessed regionally. The highest rate applied in our study is already pushing the limits for practical applications. For example, according to Filiberto and Gaunt (2013), assuming yield increase and fertiliser savings, the costs for application of 25 t ha^{-1} biochar rate in agricultural fields may not be economically feasible under current US$ circumstances. Besides the differences in the rate of biochar used, studies are frequently conducted under artificially controlled conditions and did not evaluate the effect on plant biomass. One of the exceptions is Asai et al. (2009), who tested the effect of a wood residue biochar on saturated hydraulic conductivity accompanied by measurements on rice yield. They found an increase in saturated hydraulic conductivity with application of 16 t ha^{-1} biochar in the 0–5 cm surface of a silt loam soil, but no effect on rice yield.

According to a meta-analysis done by Jeffery et al. (2011) biochar application generally leads to a 10 % increase in crop yields, although causes are poorly quantified and effects differ between crops. We observed no response of rice GY to biochar application rate during both seasons under assessment (Table 3). Yet, in S2, GFI and GP, which are yield components strongly sensitive to water stress (Fageria, 2001), increased with biochar rate higher than 16 t ha^{-1}. In rain fed systems soil matric potential can drop below −100 kPa any time during the growing season. The associated water stress leads to a reduction in overall water use efficiency by rice (Wopereis et al., 1996). Therefore, we defined a rice stress free available water content as the soil moisture content between −6 and −100 kPa (RAW). We observed an increase of 32 % in RAW with the addition of 32 t ha^{-1}, which is equivalent to 17 to 18 mm in the upper 5–10 cm layer of the sandy soil. This additional amount of water would be sufficient to satisfy the crop demand for approximately 4 additional days without rainfall, considering that the evapotranspiration rate in an uncovered soil is ca. 5 ± 0.5 mm day^{-1} during the critical stage of rice production under aerobic conditions (around 45 to 75 DAE) in the Brazilian savannah (Stone and Moreira, 2005). During the critical period for rice production in seasons under assessment in this study, in January/February 2011 (S2) and

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January/February 2012 (S3), the amount of rainfall was high ($\sim$ 650 mm) and twice the amount during the critical period in previous seasons, in February/March 2009 and January/February 2010 (Fig. 1). If there is a positive effect of biochar on RAW of a sandy soil, the effect on rice GY would be a consequence of lower precipitation rate, such as in the first seasons of the trial reported by Petter et al. (2012). Throughout the latest 32 years (from 1979 to 2013) average precipitation rate during the months of January and February in the municipality where the field trial is located was 507 mm and the frequency of an amount of rainfall lower than 650 mm was 81 % (Agritempo, 2014). In other words, in this region of Brazil's tropical savannah, rainfall during the critical period for rice production is frequently lower than 650 mm. This means that application of biochar could be sound agronomic practice that could reduce water stress and improve yield stability.

Finally, we have demonstrated that NLM can be used as an innovative analytical tool to model SWRC and compare the shape parameters α and n via formal tests. By using a NLM model, we were able to account for the random effect of latent variables related to measurements taken in the same sample unit within a specific location (plot), leading to a reduction in the uncertainty of estimation of the SWRCs (Fig. 3). By using the SAS program, results of model fitting were generated by year and soil layer in one run, facilitating the management of the large data set.

5 Conclusions

We found a consistent increase in plant available water and rice available water in the upper soil layer with around 0.8 % and 1 % for each t ha^{-1} of biochar amendment, respectively, at 2 and 3 years after application. The impact on water retention capacity of the sandy soil is mostly related to an increment in overall porosity of the soil matrix and did not result in increased rice yield, most likely because rainfall during critical period for rice production exceeded 650 mm. The use of biochar as a soil amendment could be a worthwhile strategy to improve yield stability under water limited seasons. These

findings call for longer term field trials with feasible amounts of biochar application, which are usually lower than those applied in artificially controlled studies. In addition, detailed analyses of all biochar properties should become a standard procedure in order to better target its use as a soil amendment; different sources and methods of
5 creating biochar can lead to very different char properties. Important properties to be reported are specific surface area and particle size. Expression of the rate of biochar on a dry mass basis can also facilitate comparison of findings. In addition to our main findings, we also demonstrated the utility and adequacy of the nonlinear mixed modelling to make statistical inferences on SWRCs by accounting for spatial variability and
10 expected dependencies arising from measurements taken in the same sample unit within a specific plot in the field trial.

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Table 1. Estimates of shape parameters of the Van Genutchen model fitted to represent soil water retention within 5–10 cm and 15–20 cm layers at two (S2) and three (S3) years after application of 8, 16 and 32 t ha^{-1} biochar into a sandy Dystric Plinthosol.

Treatment	Parameter estimates (5–10 cm)		R^2	Parameter estimates (15–20 cm)		R^2
	$----\alpha---$	$---n----$		$----\alpha---$	$---n---$	
			S2			
control	0.1110 (0.0533)	1.578 (0.093)	0.94	0.0344 (0.0147)	1.656 (0.088)	0.94
8	**0.0154[b] (0.0052)**	**1.882[b] (0.110)**	0.83	**0.0061[b] (0.0023)**	**1.951[a] (0.103)**	0.83
16	0.1443 (0.0725)	1.533 (0.088)	0.95	0.0760 (0.0371)	1.513 (0.075)	0.89
32	**0.0166[b] (0.0056)**	1.794 (0.089)	0.77	0.0131 (0.0055)	1.741 (0.087)	0.82
			S3			
control	0.0651 (0.0168)	1.677 (0.071)	0.97	0.0661 (0.0175)	1.653 (0.065)	0.97
8	0.0723 (0.0150)	1.738 (0.081)	0.95	0.0895 (0.0196)	1.678 (0.067)	0.97
16	0.0969 (0.0204)	1.707 (0.074)	0.98	0.1049 (0.0253)	1.675 (0.075)	0.96
32	0.0622 (0.0110)	1.781 (0.078)	0.97	0.0410 (0.0113)	1.636 (0.052)	0.94

Standard error of estimates are within brackets ($n = 4$). Nominal significance level of t test for contrasts between control and treatments with biochar within season and soil layer: [a] $p \leq 0.05$ and [b] $0.05 < p \leq 0.10$; R^2: the squared Pearson correlation coefficient between measured and predicted soil moisture means ($n = 24$).

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Table 2. Response of key physical hydric variables to biochar rate (char) at two (S2) and three (S3) years after application in a sandy Dystric Plinthosol soil.

Variable	Fitted model (5–10 cm)	R^2	Fitted model (15–20 cm)	R^2
			—S2—	
BD	1.5923	0.00	$1.6388 + 0.0049\,\text{char}^{[c]} - 0.0001\,\text{char}^{2\,[c]}$	0.95
θ_s	0.5709	0.00	0.5395	0.00
θ_r	0.1937	0.00	0.2457	0.00
MAC	0.2006	0.00	0.1266	0.00
RAW	$0.1290 + 0.0013\,\text{char}^{[c]}$	0.21	0.1234	0.00
PAW	$0.1766 + 0.0015\,\text{char}^{[b]}$	0.34	0.1672	0.00
			—S3—	
BD	1.5651	0.00	1.6409	0.00
θ_s	$0.5675 + 0.0027\,\text{char}^{[a]}$	0.99	0.5897	0.00
θ_r	0.1785	0.00	0.2046	0.00
MAC	$0.2118 + 0.0019\,\text{char}^{[b]}$	0.76	$0.1919 + 0.0053\,\text{char}^{[c]} - 0.0002\,\text{char}^{2\,[b]}$	0.91
RAW	$0.1349 + 0.0013\,\text{char}^{[a]}$	0.89	0.1290	0.00
PAW	$0.1772 + 0.0013\,\text{char}^{[b]}$	0.91	0.1698	0.00

Rate of biochar (0, 8, 16 and 32 t ha^{-1}). Soil bulk density (BD, g cm^{-3}), saturated soil moisture (θ_s), residual soil moisture (θ_r), macro porosity (MAC: $\hat{\theta}_0 - \hat{\theta}_6$), rice available water (RAW: $\hat{\theta}_6 - \hat{\theta}_{100}$) and plant available water (PAW: $\hat{\theta}_6 - \hat{\theta}_{1500}$). ($\hat{\theta}_k$) correspond to the soil moisture content (cm^3 cm^{-3}) at a matric potential k, estimated via nonlinear modeling of soil water retention curves (Fig. 4). Nominal significance level of t tests for the biochar effect: [a] $p \le 0.01$, [b] $p \le 0.05$, [c] $p \le 0.10$; R^2: the squared Pearson correlation coefficient between measured and estimated means ($n = 4$).

Table 3. Response surfaces representing the effect of biochar (char) and N-fertilisation (N) rates on total shoot dry matter (TDM, $t\,ha^{-1}$), grain yield (GY, $t\,ha^{-1}$), harvest index (HI) and yield components of aerobic rice at two (S2) and three (S3) years after application in a sandy Dystric Plinthosol.

Variable	Fitted model	R^2
	$-------------$ S2 $-------------$	
TDM	2.10	0.00
GY	1.15	0.00
HI	$0.51 + 0.00172\,N$ [b] $-0.00003\,N^2$ [a]	0.53
PAN	$109 + 0.9824\,N$ [a] $-0.0095\,N^2$ [b]	0.27
GP	$91 - 1.62735\,char$ [b] $+ 0.04248\,char^2$ [c]	0.18
GFI	$0.81 - 0.0049\,char$ [b] $-0.00066\,N$ [a] $+ 0.00014\,char^2$ [b]	0.50
GW	$25.56 - 0.03206\,N$ [a]	0.32
	$-------------$ S3 $-------------$	
TDM	$2.22 + 0.0432\,N$ [a] $-0.00044\,N^2$ [a]	0.62
GY	$0.49 + 0.002156\,N$ [c]	0.20
HI	0.18	0.00
PAN	$146 + 0.8117\,N$ [b] $-0.01292\,N^2$ [a]	0.56
GP	132	0.00
GFI	$0.47 + 0.00155\,N$ [a]	0.32
GW	$24.99 - 0.00961\,N$ [c]	0.19

Rates of biochar (0, 8, 16, $32\,t\,ha^{-1}$) and N-fertilisation (0, 30, 60, $90\,kg\,ha^{-1}$). PAN: number of panicles m^{-2}; GP: number of grains panicle^{-1}; GFI: grain filling index; GW: 1000-grain weight (g). Nominal significance level of t tests for the effects of biochar and N: [a] $p \leq 0.01$, [b] $p \leq 0.05$, [c] $p \leq 0.10$; R^2: the Pearson correlation coefficient between observed and estimated means ($n = 16$).

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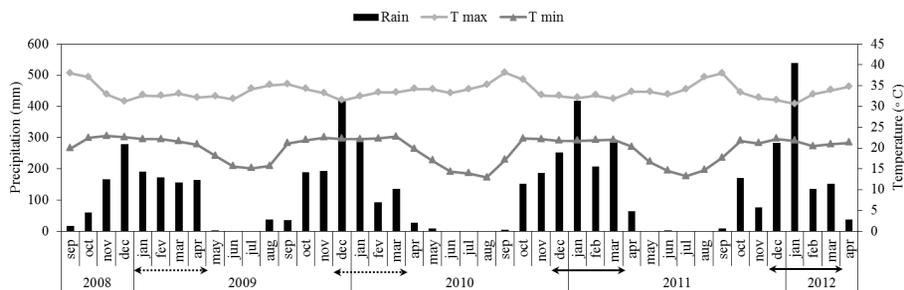
Fig. 1. Monthly precipitation (rain) and average of maxima (T max) and minima (T min) temperatures since application of biochar in the field trial in Nova Xavantina, MT, Brazil. Solid arrows indicate rice growing seasons S2 and S3. Dotted arrows represent previous seasons reported by Petter et al. (2012).
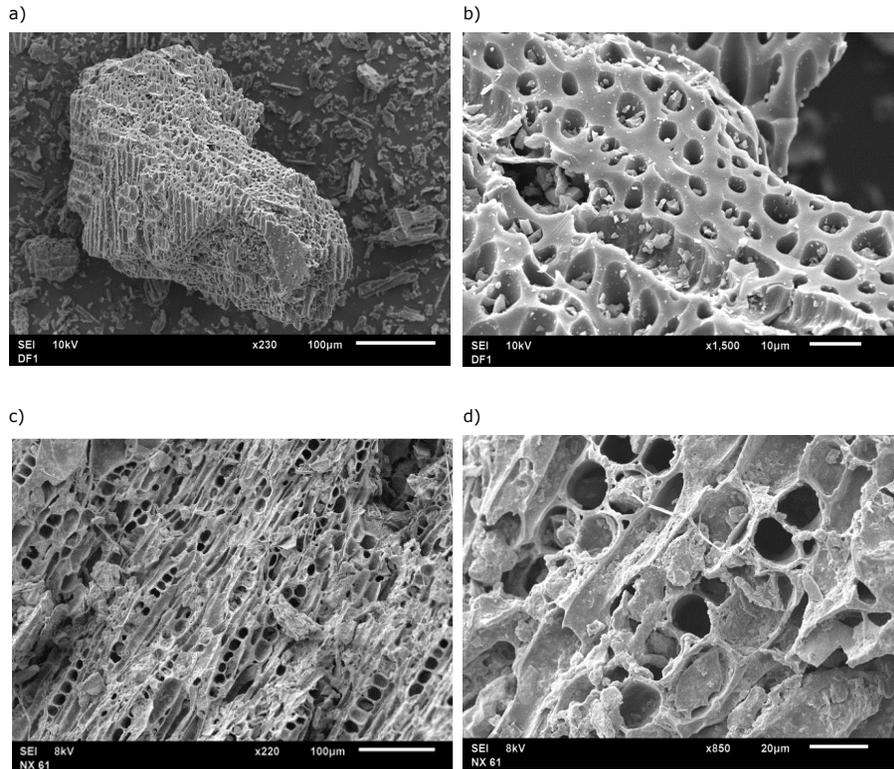
Fig. 2. High resolution images of Eucalyptus wood biochar (particle size ≤ 2000 µm) before application **(a, b)** and 2 years after application into a sandy Dystric Plinthosol **(c, d)**.
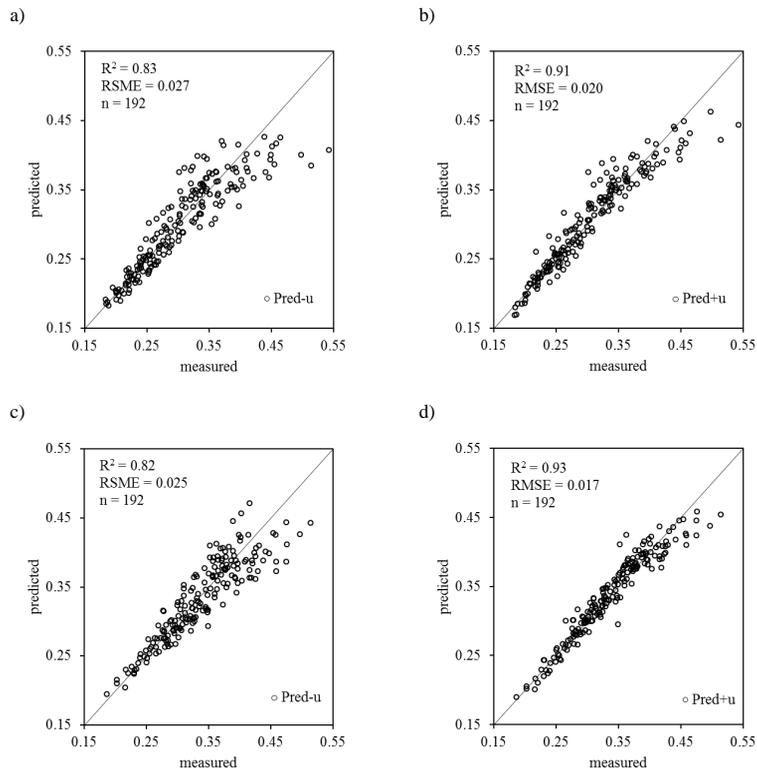
Fig. 3. Goodness of fit of the nonlinear mixed model used to predict soil water retention capacity, summarized via correlation coefficient (R^2) and root of mean square error (RMSE). Agreement between measured and predicted moisture values **(a, c)**; agreement between measured and predicted moisture values including the random effect u in the model **(b, d)**. Data measured in two years and two soil layers: 5–10 cm **(a, b)** and 15–20 cm **(c, d)**.
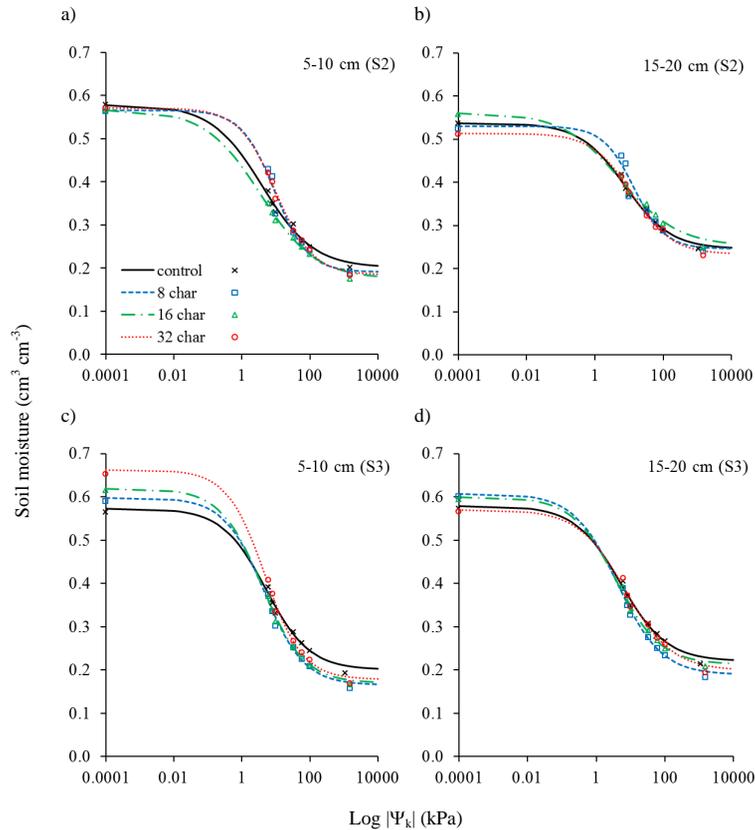
Fig. 4. Predicted (lines) soil water retention curves and measured soil moisture (symbols) at a matric potential k ($k = 0$, -6, -8, -10, -33, -60, -100 and $-1500\,\text{kPa}$) within 5–10 cm **(a, c)** and 15–20 cm **(b, d)** layers obtained at two (S2 – **a, b**) and three (S3 – **c, d**) years after application of biochar (8, 16 and $32\,\text{t ha}^{-1}$) in a sandy Dystric Plinthosol. Estimates of shape parameters are presented in Table 1.

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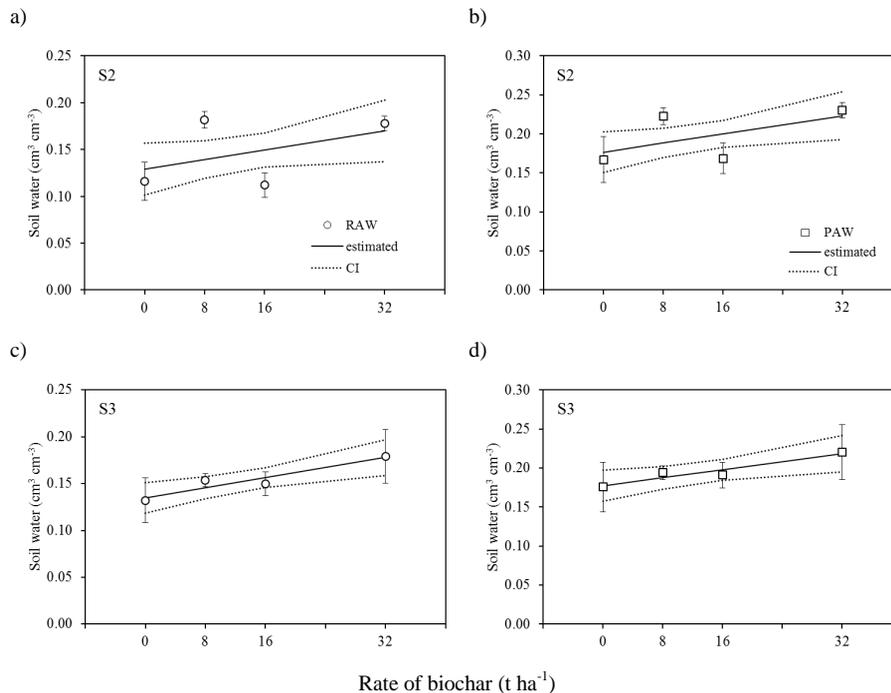
Fig. 5. Rice available water (○ RAW: $\hat{\theta}_6 - \hat{\theta}_{100}$) and plant available water (□ PAW: $\hat{\theta}_6 - \hat{\theta}_{1500}$) in the upper 5–10 cm layer of a sandy Dystric Plinthosol at two (S2 – **a**, **b**) and three (S3 – **c**, **d**) years after application of biochar rate (0, 8, 16 and 32 t ha^{-1}). Symbols represent means of soil moisture content and error bars represent standard errors ($n = 4$). Solid lines represent estimated responses to biochar rate with respective 95 % confidence intervals (CI, dotted lines). Parameter estimates of fitted linear models are presented in Table 2.

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