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Phytolith-rich biochar increases cotton biomass and silicon-mineralomass in a highly weathered soil

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3 1 **Phytolith-rich biochar increases cotton biomass and silicon-mineralomass in a highly**
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5 2 **weathered soil**
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3 **15 Abstract**
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7 16 Non-essential silicon (Si) is beneficial to plants. It increases the biomass of Si-accumulator plants by
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9 17 improving photosynthetic activity and alleviating stresses. Desilication, however, takes place because of
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11 18 natural soil weathering and removal of harvested biomass. Pyrolysis transforms Si-rich biomass into
12
13 19 biochar that can be used to supply bioavailable Si.
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16 20 Here, we applied two biochar materials differing in Si content on soils differing in weathering stage: a
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18 21 young Cambisol and a highly weathered Nitisol. We studied the impact of biochar supply on the
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20 22 bioavailability of Si, cotton biomass and Si mineralomass. The biochar materials derived from,
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22 23 respectively: *Miscanthus x giganteus* –Mi– (34.6 g Si kg⁻¹ in biochar) and soft woody material –SW– (0.9
23
24 24 g Si kg⁻¹ in biochar). They were compared to conventional Si fertilizer wollastonite –Wo– (CaSiO₃).
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26 25 Amendments were incorporated in soils at the rate of 3% (w/w). The content of bioavailable Si in soil was
27
28 26 determined through 0.01 M CaCl₂ extraction.
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31
32 27 In the Cambisol, the proportion [CaCl₂ extractable Si: total Si content] was significantly smaller for Mi
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34 28 (0.9%) than for Wo (5.2%). In the Nitisol, this proportion was much larger for Mi (1.4%) than for Wo
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36 29 (0.7%). Mi-biochar significantly increased Si-mineralomass relatively to SW-biochar in both soils. This
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38 30 increase was, however, much larger in the Nitisol (5.9-fold) than in the Cambisol (2.2-fold).
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42 31 Mi biochar is thus an alternative Si fertilizer to Wo to supply bioavailable Si, increase plant biomass, and
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44 32 promote the biological cycle of Si in the soil-plant system in the Nitisol. Besides, it increased soil fertility
45
46 33 and soil organic carbon content.
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49 34 **Keywords** biochar, bioavailable silicon, soil desilication, cotton
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36 Introduction

37 Silicon (Si) is ubiquitous in rocks and soils. Si is not essential, but beneficial to plants. It increases
38 photosynthetic activity and plant resistance against various biotic and abiotic stresses (*Belanger, 1995;*
39 *Fauteux et al., 2005; Liang et al., 2007*). Aqueous monosilicic acid (H_4SiO_4^0) is ubiquitous in soil solution
40 where plant roots take it up. In plants, mass flow transports H_4SiO_4^0 upwards to transpiration sites.
41 Therein, water loss increases H_4SiO_4^0 concentration, and induces polymerization through Si-O-Si bounds,
42 and further precipitation of hydrated amorphous silica as phytoliths (amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$) (*Epstein,*
43 *1994; Ma et al., 2006*). Phytoliths (PhSi) are major biogenic silicate minerals (BSi). They return into the
44 topsoil with dead plant materials, and further contribute to the pool of dissolved Si (DSi) in soil (*Keller et*
45 *al., 2012*) because of their solubility (*Fraysse et al., 2009*). They thus supply the pool of bioavailable Si in
46 soils under forests (*Cornelis et al., 2011; Gérard et al., 2008*), grasslands (*Alexandre et al., 2011; Blecker*
47 *et al., 2006; Issaharou-Matchi et al., 2016; White et al., 2012*) and croplands either in temperate conditions
48 (*Vandevenne et al., 2015*) or in the humid tropics (*Henriet et al., 2008*). The contribution of PhSi to DSi
49 pool can be substantially impacted by land use (*Barão et al., 2014; Struyf et al., 2010*), harvest exportation
50 (*Keller et al., 2012; Vandevenne et al., 2015; Vandevenne et al., 2012*), soil weathering stage (*Henriet et*
51 *al., 2008*) and, overall, soil processes (*Cornelis and Delvaux, 2016*).

52 The regular removal of straws of high-Si accumulator plants combined with natural desilication in freely
53 drained soils leads to a substantial decrease of PhSi and DSi pools in agroecosystems (*Keller et al., 2012;*
54 *Struyf et al., 2010; Vandevenne et al., 2015*). Si supply may therefore be required to sustain continuous
55 cropping in highly desilicated soils depleted in weatherable silicate minerals. The use of traditional
56 amendments raises cost and environmental problems (*Berthelsen et al., 2001; Haynes, 2014; Haynes et al.,*
57 *2013; Datnoff and Heckman, 2014*), prompting us to develop other ways to improve the use of available
58 biomass.

59 Biochar is a black carbon used as a soil amendment. It is produced by heating organic matter under

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3 60 oxygen-limited conditions. Pyrolysis converts organic substances into stable C compounds, hence
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5 61 preserves atmospheric C (Lehmann and Joseph, 2015; Lehmann et al., 2011). Applied to soil, biochar
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7 62 retains and supplies plant nutrients (Glaser et al., 2002; Laird et al., 2010; Lehmann et al., 2003), increases
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9 63 soil C stock (Lehmann and Joseph, 2015), soil pH and plant growth (Biederman and Harpole, 2013).
10
11 64 Black carbon significantly increases soil cation exchange capacity (CEC) through its large surface charge
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13 65 density and surface area (Liang et al., 2006). Yet the effect of biochar on plant growth largely depends on
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15 66 soil properties and biochar types (Biederman and Harpole, 2013; Crane-Droesch et al., 2013; Jeffery et
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17 67 al., 2011).

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21 68 Pyrolysis of plant residues concentrates PhSi minerals (Houben et al., 2014) which in turn contribute to
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23 69 supply DSi (Houben et al., 2014; Xiao et al., 2014), and increase Si uptake by plants (Liu et al., 2014). The
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25 70 impact of both the PhSi content of biochar and soil silicon availability on plant growth and Si uptake is,
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27 71 however, unknown. Here, we used two biochars differing in Si content, and apply them on soils differing
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29 72 in weathering stage, respectively, a young Cambisol and an old, highly weathered, Nitisol. We studied the
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31 73 release of DSi after biochar application. We further investigated the effect of biochar on soil fertility, plant
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33 74 biomass and Si mineralomass, and compared it to the one of CaSiO₃-wollastonite.

34 35 36 37 75 **Materials and methods**

38 39 40 76 ***Biochar, wollastonite and soils***

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43 77 Biochars and wollastonite. The biochars were produced by industrial pyrolysis (550°C, heating rate
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45 78 65 °C/min, kiln residence time 12 min) at UK Biochar Research Centre (UKBRC), respectively from
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47 79 *Miscanthus* (*Miscanthus x giganteus*) –Mi– and soft wood (Mixed softwood pellets) –SW– (Table 1). The
48
49 80 wollastonite –Wo– was provided by R.T Vanderbilt Company, Inc. (Norwalk, CT, USA) (Table 1). In the
50
51 81 following text, the biochars and wollastonite are considered as soil amendments.

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55 82 Soils and soil:amendment mixtures. The two soils key out as, respectively, a Dystric Cambisol (CA) and a

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3 83 Rhodic Nitisol (NI) in the WRB system (IUSS, 2014). CA (Forest of Lauzelle, Louvain-la Neuve,
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5 84 Belgium) developed from quaternary calcareous silty loess under humid temperate conditions (Titeux and
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7 85 Delvaux, 2009). NI is a paleosol from the quarry of Transinne (Belgium), formed under humid tropical
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9 86 paleo-conditions. The quarry exhibits a deep 65m saprolithic profile derived from Early Devonian
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11 87 bedrock, containing kaolinite, resistant muscovite and quartz, and Fe oxyhydroxides (Thiry et al., 2006).
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13 88 The soil samples were air-dried and sieved at 2-mm. The soil:amendment mixtures were made at 100:3
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15 89 g:g (dry soil weight), and are named CA-Mi, CA-SW, CA-Wo, NI-Mi, NI-SW and NI-Wo.

18 19 90 *CaCl₂ extraction of Si*

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22 91 The extraction was carried out on the Si amendments, soils and soil:amendment mixtures before the cotton
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24 92 pot experiment. The CaCl₂-extractable Si content (CaCl₂-Si) was determined using a 5g:50ml (0.01 M
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26 93 CaCl₂) soil:solution ratio, and a 5h continuous shaking time (Haysom and Chapman, 1975). After
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28 94 centrifuged at 3,000×g for 20 min, the supernatant was separated for analysis. The residues were
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30 95 submitted to five successive extractions during 5 days. The concentration of Si was measured in each
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32 96 extract by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

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36 97 Analyses. pH was measured in, respectively, H₂O and KCl 1M, with 5g:25ml suspensions. The CEC and
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38 98 content of exchangeable cations were determined using CH₃COONH₄ 1M buffered at pH=7 (Chapman,
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40 99 1965). Elemental analysis was carried out after calcination and Li-metaborate + Li-tetraborate fusion
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42 100 (Chao and Sanzalone, 1992). The elemental contents were determined by ICP-AES. Elemental contents of
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44 101 alkaline and alkaline-earth cations were summed up as the total reserve in bases (TRB), which estimates
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46 102 the content of weatherable minerals (Herbillon, 1986). Total carbon (C) and nitrogen (N) contents were
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48 103 measured by dry combustion with a CNS analyzer (Flash EA1112 Series).

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52 104 Scanning Electron Microscopy (SEM). The analyses of biochar particles were performed on specimens
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54 105 using a JEOL FEG SEM 7600F, equipped with Energy Dispersive X-ray Spectrometry system (EDX, Jeol

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3 106 JSM2300 with a resolution < 129 eV) operating at 15 keV with a working distance of 8 mm for the
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5 107 element detection. The acquisition time for the chemical spectra lasted 100 s with a probe current of 1 nA.
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8 108 ***Plant material and analyses, pot experiment***

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11 109 Cotton plant. We used *Gossypium hirsutum*, var (STAM 59A-Bollgard II) from southern Burkina Faso.
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15 110 Pot experiment in a phytotron (5 months). The soil:amendment mixtures (100:3 g:g) were irrigated with
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17 111 deionized water and allowed to equilibrate for a week at 70% of field water holding capacity before
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19 112 planting. After germination in deionized water, the plantlets were allowed to grow up to 5-cm. They were
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21 113 then transplanted into pots (7.5 L) containing the respective soil:amendment mixtures (3kg dry weight), in
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23 114 triplicate under 28°C and relative humidity at 80%. Each pot was watered every three days with 33 ml
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25 115 deionized water during the first two months, and 100 ml the last three months. No nutrients were supplied.
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27 116 We collected the aboveground plant part after 5 months for further drying at 55°C during 7 days prior to
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29 117 biomass weighing.
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33 118 Analyses. Mineral analysis was carried out after calcination at 450°C for 1 day and fusion in Li-
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35 119 metaborate + Li-tetraborate at 1,000°C (Chao and Sanzalone, 1992), followed by ash dissolution with
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37 120 concentrated HNO₃. Element contents were measured by ICP-AES. Element mineralomass was computed
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39 121 from total element contents and cotton biomass.
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42 122 ***Statistical analyses***

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46 123 We used the SPSS 17.0 statistical software to carry out the one-way analysis of variance (ANOVA) (at
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48 124 $p < 0.05$ level) and LSD (at $p < 0.05$ level).
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51 125 **Results**

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54 126 *Properties of the biochars and wollastonite*
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3 127 As shown in Table 1, the OC content (%) was 84.9 in SW, 77.1 in Mi and 0.6 in Wo. The total N content
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5 128 (%) was 1.2 in SW and 2.0 in Mi. The contents of CaCl_2 extractable Si (g kg^{-1}) were larger in Mi (11.4)
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7 129 than in Wo (8.8) and SW (0.01). Si content of Wo amounted to 233.3 g kg^{-1} which was 7 times larger than
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9 130 that of Mi (34.6 g kg^{-1}), and 259 times larger than in SW (0.9 g kg^{-1}). The contents of Ca, Mg in Wo were
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11 131 also significantly larger than in Mi and WS. The contents of K ($\text{cmol}_c \text{ kg}^{-1}$) were larger in Mi (14.9) than
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13 132 in SW (2.6) and Wo (1.1). Figure 1 illustrated the SEM micrographs and associated EDX spectra of
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15 133 biochar materials SW and Mi. In particular, Fig. 1(f) showed the occurrence of dumbbell-shaped, fine silt-
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17 134 sized phytoliths in Mi biochar. As inferred from Fig.1 (e), they were abundant and undamaged after
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19 135 pyrolysis at $550 \text{ }^\circ\text{C}$.

23 136 *Soil and soil:amendment properties*

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26 137 CA and NI are acid soils since their pH_{water} values were 4.6 and 5.2, respectively (Table 2). C and N
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28 138 contents, CEC and contents of exchangeable cations were larger in CA than in NI. Of course, biochar
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30 139 application resulted in a huge increase in C content while Wo did not. The latter application led to a
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32 140 marked increase in pH and content of exchangeable Ca. SW application did not generate any change of
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34 141 pH, CEC, contents of exchangeable cations and base saturation whatever the soil type. To the contrary, Mi
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36 142 application induced a significant increase of these parameters. In particular, exchangeable K content
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38 143 ($\text{cmol}_c \text{ kg}^{-1}$) increased from, respectively 0.2 to 0.97 in CA, and 0.05 to 0.81 in NI. From Total contents of
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40 144 Al and Fe (g kg^{-1}) amounted to, respectively, 39.2 and 18.5 in CA, 96.5 and 30.6 in NI (Table 3). Total Si
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42 145 content (g kg^{-1}) in CA and NI was 376.8 and 311.9, respectively. Computed values of $\text{Si}/(\text{Al}+\text{Fe})$ atomic
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44 146 ratio were thus larger in CA (7.5) than in NI (2.7). TRB ($\text{cmol}_c \text{ kg}^{-1}$) amounted to 112 in CA and 99 in NI.
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46 147 Residual weatherable minerals in CA were plagioclase and feldspar, and soil clay minerals. From Figure 2,
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48 148 CA clay minerals consisted of kaolinite and an assemblage of 2:1:1 and 2:1 clay minerals involving
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50 149 chlorite, illite, vermiculite and smectite. NI distinctly differed by the large dominance of well crystallized
51
52 150 muscovite and kaolinite. In the Nitisol, K was by far the largest dominant cation in TRB, in line with the
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54 151 occurrence of muscovite, a dioctahedral mica resistant to weathering. The large amount of non-
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3 152 exchangeable K (Table 3) thus hid the advanced weathering stage of NI because muscovite is stable and
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5 153 does not weather in soils. The reserve of weatherable minerals was then estimated by the difference
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7 154 between TRB and the content of non-exchangeable K, excluding K-bearing muscovite. [TRB-K] (cmol_c
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9 155 kg⁻¹) amounted to 72.5 in CA and 22.1 in NI, indicating the strongly advanced weathering stage of NI.
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11 156 [TRB-K] did not increase following biochar application. To the contrary, wollastonite application
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13 157 generated a marked increase of total Ca content (cmol_c kg⁻¹): from 15 to 63 in CA, and from 1 to 48 in NI.
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15 158 Cumulative CaCl₂-Si (mg kg⁻¹) (Table 3, Figure 3) was significantly larger in CA (34) than in NI (24).
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17 159 CaCl₂-Si significantly ($p < 0.01$) increased after Wo application in CA (398.7) and NI (71.7). Unlike SW,
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19 160 Mi significantly ($p < 0.01$) increased CaCl₂-Si in CA (43.2) and NI (38.5).
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23 161 *Biomass and mineralomass of cotton plants*

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25
26 162 The cotton biomass (g plant⁻¹) was significantly larger in CA (8.6) than in NI (0.32) (Table 4). Mi
27
28 163 significantly increased cotton biomass, by 84% in CA, and 368% in NI. Mi significantly increased plant
29
30 164 mineralomass of Ca, K and Mg in both soils. Plant Si mineralomass (mg plant⁻¹) was, by far, significantly
31
32 165 larger in CA (10.6) than in NI (0.8). Relatively to SW, Mi significantly increased the plant Si content (g Si
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34 166 kg⁻¹ DW): 0.65 for CA-Mi and 0.74 for NI-Mi, as well as plant Si mineralomass (mg Si plant⁻¹): 10.52 for
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36 167 CA-Mi and 1.12 for NI-Mi). Si mineralomass indeed increased by 120% in CA-Mi and 180% in NI-Mi
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38 168 relatively to the untreated soils CA and Mi.
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42 169 **Discussion**

43 44 45 46 170 *Weathering stage of soils*

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49 171 The values of TRB and Si/(Al+Fe) ratio as well as the nature of secondary clay minerals are used to
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51 172 assess soil weathering stage (Herbillon, 1986). Taking into account the stability of muscovite in soils, NI
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53 173 exhibited an advanced weathering stage characteristic of strongly weathered ferrallitic soils (Herbillon,
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55 174 1986). In CA, the large dominance of quartz is characteristic of soils of the Belgian loess belt, in which the
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3 175 reserve of weatherable minerals is concentrated in the clay fraction (*Brahy et al., 2000*). CA soil clay
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5 176 minerals (kaolinite, chlorite, illite, vermiculite and smectite: Figure 2a) revealed a mineralogical
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7 177 assemblage typical of moderately weathered soils under temperate climates. To the contrary, NI soil clay
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9 178 minerals (Figure 2b) make an assemblage typical for desilicated, highly weathered soils formed under
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11 179 humid tropical conditions. Consequently, CaCl₂-Si content was significantly larger in CA than in NI
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14 180 (Figure 3).

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17 181 *Mobility of Si in soil: amendment mixtures*

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20 182 As it is linked to the DSi pool from which plant roots take up Si, CaCl₂-Si could quantify the pool of
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22 183 bioavailable Si in soils (*Sauer et al., 2006*). Cumulative CaCl₂-Si (mg kg⁻¹) was significantly larger in
23
24 184 soil:Wo (398.7 in CA-Wo, 71.7 in NI-Wo) than in soil:biochar CA-Mi (43.2), NI-Mi (38.5), CA-SW
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26 185 (30.9) and NI-SW (24.1) (Table 3; Figure 3). Wo is indeed an efficient Si fertilizer releasing bioavailable
27
28 186 Si. For each amendment, CaCl₂-Si was systematically smaller in NI:amendment mixtures. Part of H₄SiO₄^o
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30 187 released by amendments was undoubtedly adsorbed by oxide surfaces in NI as it commonly occurs in
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32 188 highly weathered soils (*Herbillon et al., 1977*).

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35
36 189 To further assess Si mobility, we define the efficiency of each amendment (AM) using CaCl₂-Si and total
37
38 190 Si contents (Table 3) as follows:

$$\frac{[\text{CaCl}_2 - \text{Si in soil: AM}] - [\text{CaCl}_2 - \text{Si in soil}]}{\text{Total Si content of AM}} \times 100$$

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46 191 In CA, the efficiency of MI was significantly smaller (0.9%) than that of Wo (5.2%). To the contrary, in
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48 192 NI, Mi efficiency was larger (1.4%) than to the one of Wo (0.7%). Possibly phytolith solubility could be
49
50 193 larger in NI-Mi, because of a larger pH. Besides, the release of bioavailable Si was significantly larger for
51
52 194 Mi than for SW (Figure 3 c, d). The ample reserve of PhSi in Mi vs SW (34.6 vs 0.9 g Si kg⁻¹, Table 1) and
53
54 195 the accessibility of phytoliths in Mi (Figure 1 e, f) support that phytoliths readily contribute to DSi. They
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3 196 resist to pyrolytic temperatures as high as 550°C, and further dissolve to release DSi given their solubility
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5 197 (*Fraysse et al.*, 2009). Since their dissolution rate increases with increasing pH in the range of pH 3-12
6
7 198 (*Fraysse et al.*, 2006), the ability of phytolith-rich Mi to supply DSi is enhanced by pH increase, especially
8
9 199 in NI, where silica sorption increased pH of surrounding solution. Indeed, Fe oxides adsorb Si in soils
10
11 200 (*Jones and Handreck*, 1963, 1967) and control DSi (*McKeague and Cline*, 1963).
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15 201 The release of bioavailable Si in Mi-amended soils was not affected by soil type and weathering stage.
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17 202 The biochar derived from high-Si accumulator *Miscanthus* is thus an alternative Si fertilizer to
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19 203 wollastonite to supply bioavailable Si in the highly weathered Nitisol.
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22 204 *Effect of biochar amendment on soil properties*

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25 205 As already reported (*Sohi et al.*, 2010; *Van Zwieten et al.*, 2010), biochar application to soils affects their
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27 206 properties (Table 2). The impact depends, however, on the types of biochar and soil. Supplying ash
28
29 207 biochar induces a change of pH and nutrient availability, (*Clarholm*, 1994; *Mahmood et al.*, 2003). Here,
30
31 208 applying biochar did not significantly modify CEC in CA. However, it slightly increased CEC in NI, but
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33 209 only after Mi application, which also increased the contents of exchangeable cations, namely K and Mg in
34
35 210 CA-Mi, and Ca, K, Na and Mg in NI-Mi (Table 2). Such increases were not observed after SW addition.
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37 211 Since applying Mi increased the effective CEC (ECEC), we hypothesize that it is due to an increase of
38
39 212 surface area and surface charge density of biochar particle, as previously reported for black C (*Liang et al.*,
40
41 213 2006). The pH rise, in turn, undoubtedly led to increase ECEC (*Glaser et al.*, 2002; *Houben et al.*, 2014;
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43 214 *Laird et al.*, 2010). Relatively to SW, Mi contained more ashes and initial exchangeable and non-
44
45 215 exchangeable cations (Table 1 and Figure 1). Mi thus had a larger ability to increase pH and ECEC, as
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47 216 observed by *Houben et al.* (2014). Furthermore, the improvement of soil properties was more pronounced
48
49 217 in NI-Mi than in CA-Mi. Base saturation (BS %) significantly increased in both CA-Mi and NI-Mi,
50
51 218 reflecting the ability of Mi biochar to enhance nutrient availability (Table 3) as predicted by *Liang et al.*
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53 219 (2006) for black C. The larger BS after Mi amendment was due to the larger nutrient content (Ca, Mg and
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220 K) in Mi relatively to SW (Table 1). The impact of Mi biochar on soil fertility was thus positive,
221 particularly in the highly weathered Nitisol, though at a very low level tested in non-fertilized soil.

222 *Effect of biochar amendment on cotton biomass and Si mineralomass*

223 The amounts of available nutrients (exchangeable Ca, K and Mg) and bioavailable Si were larger in CA
224 than in NI (Tables 2 and 3). Thus, the cotton biomass and mineralomass were significantly larger in CA
225 than in NI regardless the type of biochar amendment.

226 Plant response to biochar amendment varied with the type of biochar (*Spokas and Reicosky, 2009*) and
227 application rate (*Liu et al., 2013*). Mi-biochar increased both the plant biomass and element uptake, as a
228 result of elevated nutrient availability (Ca, Mg and K). Here, both the Ca, Mg and K mineralomass and
229 soil Ca, Mg and K contents were significantly larger, respectively, in CA-Mi and NI-Mi than in CA-SW
230 and NI-SW (Table 2 and Table 4). Nutrients were likely released in soil via the degradation of labile
231 organic compounds associated with biochar (*Rajkovich et al., 2012; Topoliantz et al., 2005; Yamato et al.,*
232 *2006*). Moreover, biochar amendment promotes plant productivity through the increase of pH, which in
233 turn increases nutrient availability and/or decrease mineral toxicities (*Lehmann et al., 2003; Rondon et al.,*
234 *2007; Yamato et al., 2006*). Here, the biochar-induced increase of ECEC likely promoted plant growth and
235 biomass (Table 2 and Table 4) (*Major et al., 2010*). The marked difference of soil fertility between CA and
236 NI, discussed above, induced a huge difference in cotton biomass (g plant^{-1}): 8.8 in CA vs 0.3 in NI (Table
237 3 and Table 4). The increase of cotton biomass was 4.7 fold from NI to NI-Mi and 1.8-fold from CA to
238 CA-Mi, whereas no significant effect was measured after SW amendment. Mi-biochar induced an increase
239 of CEC and ECEC, and thus improved soil fertility in the highly weathered Nitisol, thereby promoting
240 plant growth.

241 Si uptake by cotton plants markedly differed between CA and NI (Figure 4). After Mi application, Si
242 uptake increased by 5.9-fold in NI, and 2.2-fold in CA, keeping in mind that biomass (g plant^{-1}) (0.2 – 1.5

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3 243 g.plant⁻¹) was very low in NI (0.2–1.5) compared to CA (8.8–16.2) (Table 4). As discussed above,
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5 244 phytoliths were abundant in Mi; they dissolved and released DSi, thereby contributing to the pool of
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7 245 bioavailable Si, which was readily taken up by plant roots (Figure 1, 2, 3; Table 3). This effect was
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9 246 particularly important in the highly weathered Nitisol depleted in primary and secondary silicates.
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12 247 **Conclusion**

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16 248 *Miscanthus* biochar and wollastonite amendments significantly ($p < 0.01$) enhanced the release of CaCl₂-
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18 249 extractable Si in a young Cambisol and an old, highly weathered Nitisol. Soft wood biochar amendment
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20 250 had no effect on the release of CaCl₂-extractable Si in both soils. *Miscanthus* biochar supply increased
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22 251 ECEC, particularly the content of exchangeable K, while soft wood biochar did not have any effect on
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24 252 these parameters whatever the soil type. Both biochar amendments induced a significant effect on C and N
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26 253 contents in both soils. *Miscanthus* biochar generated a significant increase of cotton biomass. That
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28 254 increase was, however, larger in the Nitisol than in the Cambisol, since it was 4.7-fold in the former and
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30 255 1.8-fold in the latter. In terms of Si uptake after Mi application, the increase in the Nitisol (5.9-fold) was
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32 256 much larger than in the Cambisol (2.2-fold), supporting a larger efficiency of Si release from *Miscanthus*
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34 257 phytoliths in the Nitisol.
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38 258 Our data thus highlight that *Miscanthus* biochar is an alternative Si amendment to wollastonite to supply
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40 259 bio-available Si, increase plant biomass and promote the biological cycle of Si in the soil-plant system.
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42 260 This positive impact of a Si-rich biochar is, however, larger in the old, desilicated, highly weathered
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44 261 Nitisol. Overall, it demonstrates that Si is progressively released from phytolith-rich biochar, and directly
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46 262 contributes to the pool of bioavailable Si for plant root uptake in soil. This is particularly important for
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48 263 agro-ecosystems in which high-Si accumulator plants grow in highly weathered, desilicated soils. Further
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50 264 field experiments are required to confirm the effect of phytolith-rich biochar as a Si fertilizer over the
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52 265 whole plant cycle. Furthermore, the efficiency of various biochar types to release Si and plant nutrients
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55 266 should be studied.
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Table 1. Selected properties of the soft wood (SW), *Miscanthus* (Mi) biochars and wollastonite (Wo): pH_{water}, total contents of Carbon (C), Nitrogen (N), CaCl₂ extractable Si (CaCl₂-Si), major alkaline and alkaline-earth cations (Ca, Mg, K, Na), and silicon (Si).

Amendments	pH	[§] C	[§] N	CaCl ₂ -Si	Ca	Mg	Na	K	Si
	H ₂ O	(%)		g kg ⁻¹	(g kg ⁻¹)				
SW	7.4	84.90	1.15	0.01(0.00)	2.79(0.79)	0.53(0.17)	0.15(0.05)	2.20(0.61)	0.77(0.22)
Mi	10.1	77.13	2.01	11.45(1.05)	6.92(0.10)	2.15(0.10)	0.58(0.03)	14.87(0.16)	34.65(0.23)
Wo	9.1	0.56	nd	8.87(1.04)	314.71(2.54)	10.80(0.06)	<0.01	1.10(0.06)	233.34(2.03)

Note: nd means not determined; [§]: Single measurements only.

Table 2. Selected physico-chemical properties of the untreated soils (Cambisol CA, Nitisol NI) and amended soils, using soft wood (CA-SW, NI-SW), *Miscanthus* (CA-Mi, NI-Mi) and wollastonite (CA-Wo, NI-Wo). The average values presented with distinct letters (a, b, c) in the Cambisol and (x, y, z) in the Nitisol are significantly different at the $p < 0.05$ level of confidence according to LSD's multiple comparison test.

Treatments	pH		C g kg ⁻¹	N	CEC	Exchangeable cations (cmol _c kg ⁻¹)				BS (%)
	H ₂ O	KCl				Ca ²⁺	K ⁺	Na ⁺	Mg ²⁺	
CA	4.62(0.02)c	3.72(0.03)c	14.12(1.32)b	1.19(0.05)a	6.67(0.31)b	2.31(0.05)b	0.20(0.02)b	0.04(0.02)c	0.39(0.01)c	44.08
CA-SW	4.72(0.00)c	3.73(0.01)c	30.95(2.38)a	1.22(0.12)a	6.14(0.82)b	2.29(0.07)b	0.22(0.02)b	0.04(0.01)c	0.39(0.01)c	47.88
CA-Mi	5.03(0.03)b	4.08(0.02)b	35.85(2.56)a	1.27(0.35)a	5.98(0.17)b	2.36(0.06)b	0.97(0.20)a	0.07(0.01)b	0.47(0.04)a	64.72
CA-Wo	6.25(0.01)a	5.36(0.02)a	14.78(1.23)b	1.11(0.03)a	8.11(0.11)a	5.42(0.13)a	0.24(0.03)b	0.10(0.01)a	0.43(0.00)b	76.32
NI	5.18(0.04)z	4.32(0.01)z	0.58(0.35)y	0.27(0.02)y	0.68(0.08)z	0.15(0.01)z	0.05(0.02)y	0.01(0.01)z	0.30(0.00)y	75.00
NI-SW	5.45(0.00)z	4.44(0.06)z	26.41(4.56)x	0.53(0.12)x	0.87(0.13)z	0.16(0.02)z	0.07(0.04)y	0.02(0.00)z	0.30(0.00)y	63.22
NI-Mi	6.25(0.10)y	5.79(0.13)y	21.29(3.69)x	0.50(0.11)x	1.04(0.07)y	0.36(0.13)y	0.81(0.55)x	0.07(0.03)x	0.37(0.05)x	154.81
NI-Wo	7.84(0.12)x	6.53(0.10)x	0.85(0.32)y	0.27(0.01)y	1.82(0.03)x	2.89x(0.23)	0.03(0.03)z	0.06(0.01)y	0.28(0.02)z	179.12

Table 3. Total contents of selected major elements and Total Reserve in Bases (TRB) in CA and NI, CA-SW, CA-Mi, CA-Wo; NI-SW, NI-Mi, NI-Wo). The average values presented with distinct letters (a, b, c) in Cambisols and (x, y, z) in Nitisols are significantly different at the $p < 0.05$ level of confidence according to LSD's multiple comparison test.

Treatments	CaCl ₂ -Si ¹ (mg kg ⁻¹)	Total Si (g kg ⁻¹)	Total elements (cmol _c kg ⁻¹)				TRB ²	[TRB-K] ³	Total elements (g kg ⁻¹)		Si/(Al+Fe)
			Ca	K	Na	Mg			Al	Fe	
CA	34.05(1.67)c	376.78	16.50	40.00	29.80	26.00	112.3	72.5	39.21	18.52	7.52
CA-SW	30.95(1.00)c	365.47	16.55	39.06	28.92	25.34	109.9	70.5	38.02	17.92	7.52
CA-Mi	43.22(1.90)b	366.50	17.08	40.00	28.99	25.34	111.4	72.4	38.01	17.93	7.54
CA-Wo	398.69(1.03)a	368.74	63.25	38.94	28.91	27.86	158.9	120.2	38.13	18.00	7.57
NI	24.03(0.68)z	311.92	1.00	77.60	7.70	13.40	99.7	22.1	96.52	30.61	2.69
NI-SW	24.11(1.04)z	302.57	1.46	75.70	7.47	13.13	97.7	22.0	93.62	29.71	2.69
NI-Mi	38.50(1.52)y	303.60	2.00	76.64	7.54	13.13	99.3	23.4	93.64	29.73	2.70
NI-Wo	71.70(2.64)x	305.84	48.16	75.57	7.46	15.64	146.8	71.3	93.73	29.72	2.72

¹: cumulative amount after 5 extractions (see also Figure 3);

²: TRB is the sum of total contents of Ca, Mg, Na and K in soil (*Herbillon*, 1986);

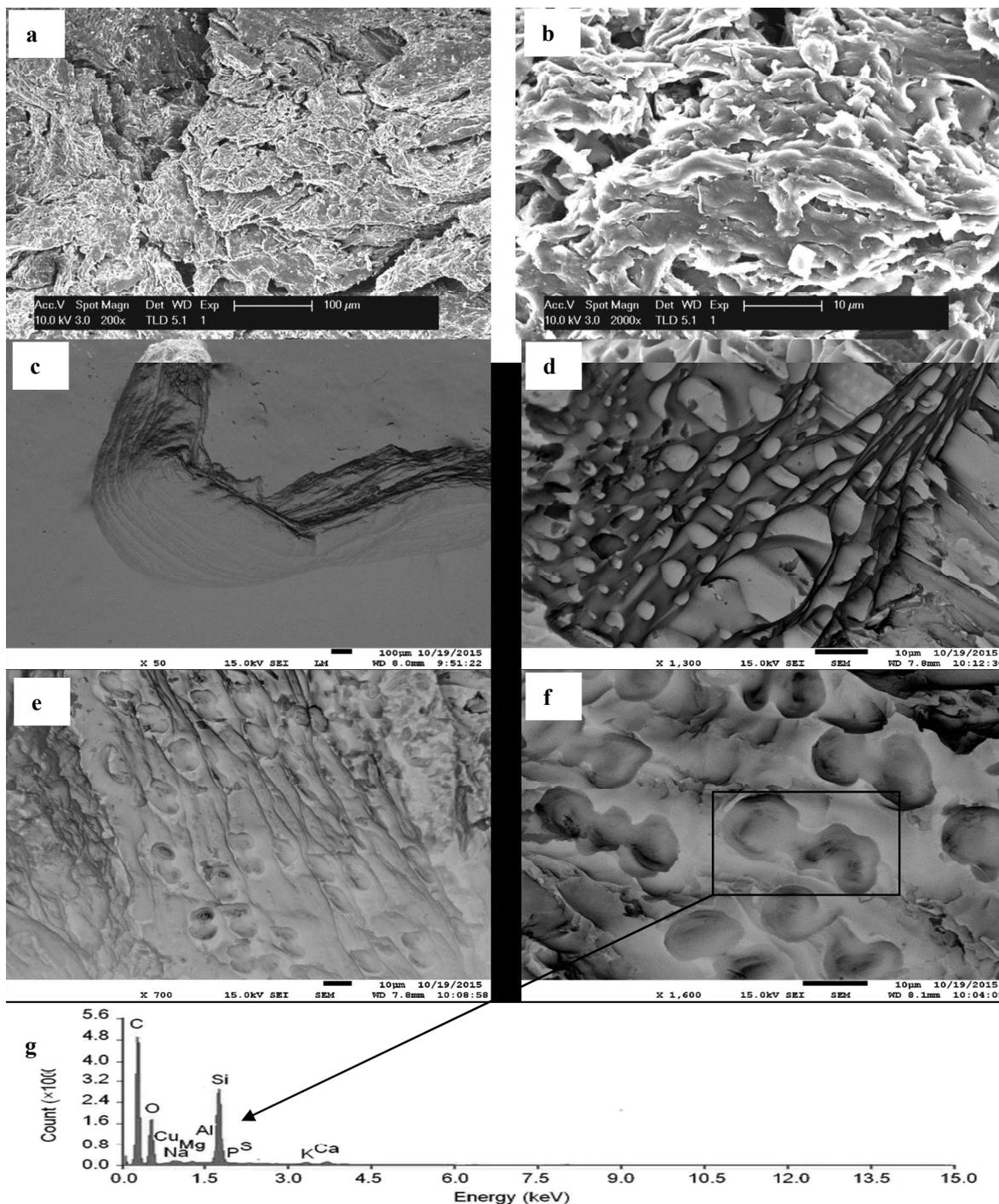
³: TRB-K is the sum of total contents of Ca, Mg and Na in soil, excluding non-exchangeable K [total K – exchangeable K], associated with resistant muscovite or oxidized biotite, both dioctahedral micaceous minerals.

Table 4. Experimental values of cotton biomass, plant contents of Ca, Mg, Na, K, and Si, and element mineralomass (i.e. uptake) in the cotton plants grown on the untreated soils (Cambisol CA, Nitisol NI), and biochar-amended soils (*Miscanthus* Mi; Soft Wood SW). The average values presented with distinct letters (a, b, c) in CA and (x, y, z) in NI are significantly different at the $p < 0.05$ level of confidence according to LSD's multiple comparison test.

Treatments		CA	CA-SW	CA-Mi	NI	NI-SW	NI-Mi
Biomass	g plant ⁻¹	8.82(1.10)b	8.63(2.51)b	16.24(2.11)a	0.32(0.07)y	0.24(0.11)y	1.51(0.40)x
Ca	g kg ⁻¹	14.64(4.59)a	7.79(0.62)b	13.22(2.05)a	3.16(1.09)y	3.82(1.39)y	11.42(2.46)x
Mg		2.76(0.48)a	2.13(0.30)b	2.48(0.27)a	1.54(0.00)y	1.30(0.10)y	2.25(0.05)x
Na		0.24(0.08)a	0.11(0.02)b	0.09(0.03)b	0.82(0.01)x	0.58(0.00)y	0.20(0.22)z
K		15.17(3.39)b	15.15(1.33)b	23.03(4.96)a	10.40(0.01)y	14.51(0.60)y	26.74(1.61)x
Si		0.54(0.16)b	0.46(0.11)b	0.65(0.03)a	0.58(0.00)y	0.54(0.00)y	0.74(0.11)x
Ca	mg plant ⁻¹	129.09(25.14)b	67.22(16.59)c	214.73(37.52)a	1.01(0.22)y	0.92(0.65)y	17.24(4.52)x
Mg		24.35(7.27)bc	18.42(3.05)c	40.25(2.64)a	0.49(0.11)y	0.31(0.16)y	3.41(0.89)x
Na		2.09(0.84)a	0.92(0.32)c	1.53(0.44)b	0.26(0.05)xy	0.14(0.07)y	0.30(0.07)x
K		133.76(45.57)b	130.78(28.06)b	374.05(79.87)a	3.33(0.72)y	3.48(1.73)y	40.38(10.59)x
Si		4.76(0.32)b	3.93(0.21)c	10.52(2.30)a	0.19(0.05)y	0.13(0.07)y	1.12(0.12)x

444

445 **Figures**



449 **Figure 1.** Scanning electron micrographs (SEM) images of biochar materials from soft wood (a, b), and
 450 *Miscanthus* (*Miscanthus* × *giganteus*) straws (c, d). e and f are the SEM images of *Miscanthus*
 451 phytoliths. The energy dispersive X-ray spectra (EDX) (g) collected from f, shows the
 452 dominance of C, O and Si, hence documenting the presence of phytoliths (SiO₂·nH₂O).
 453
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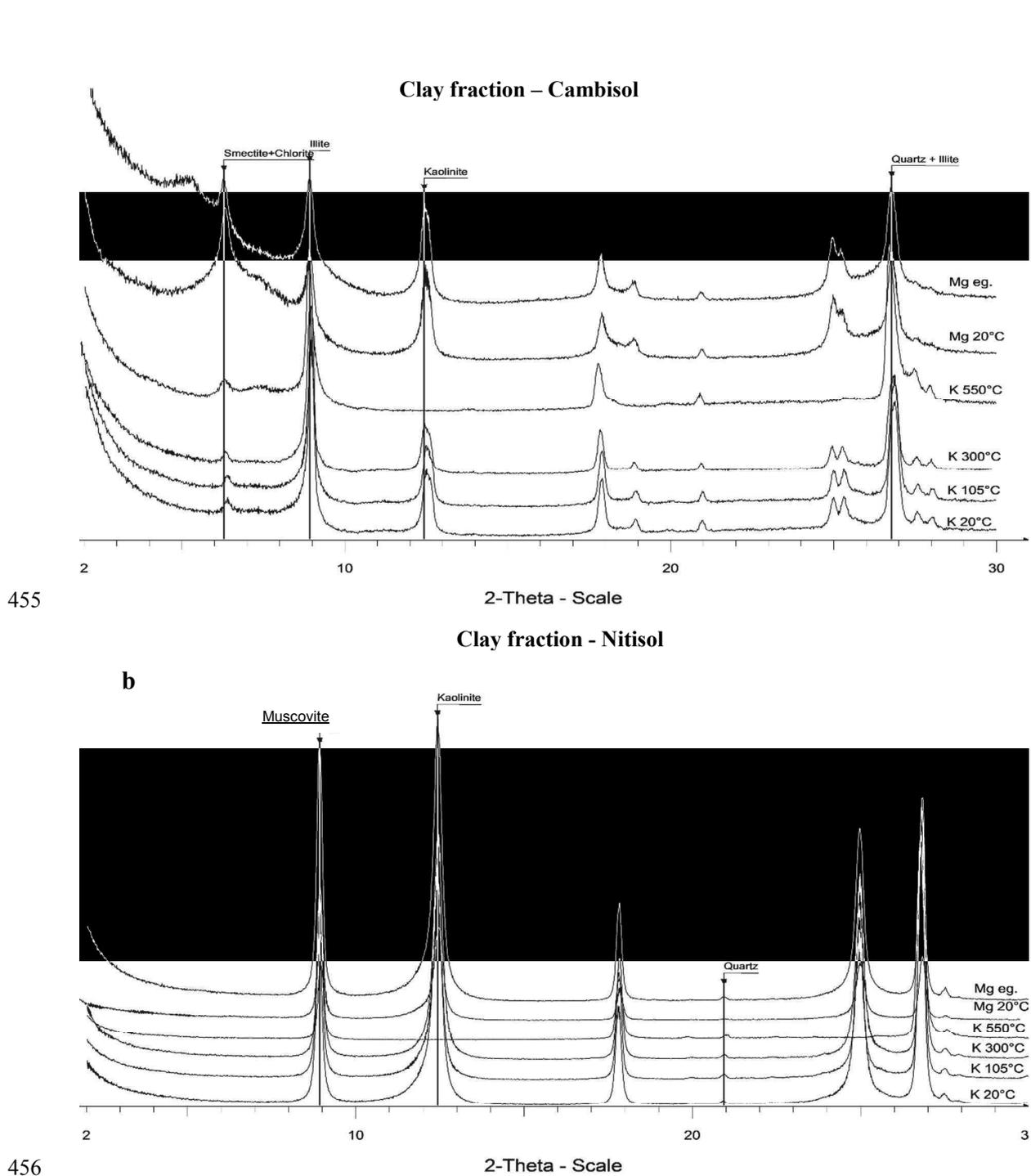
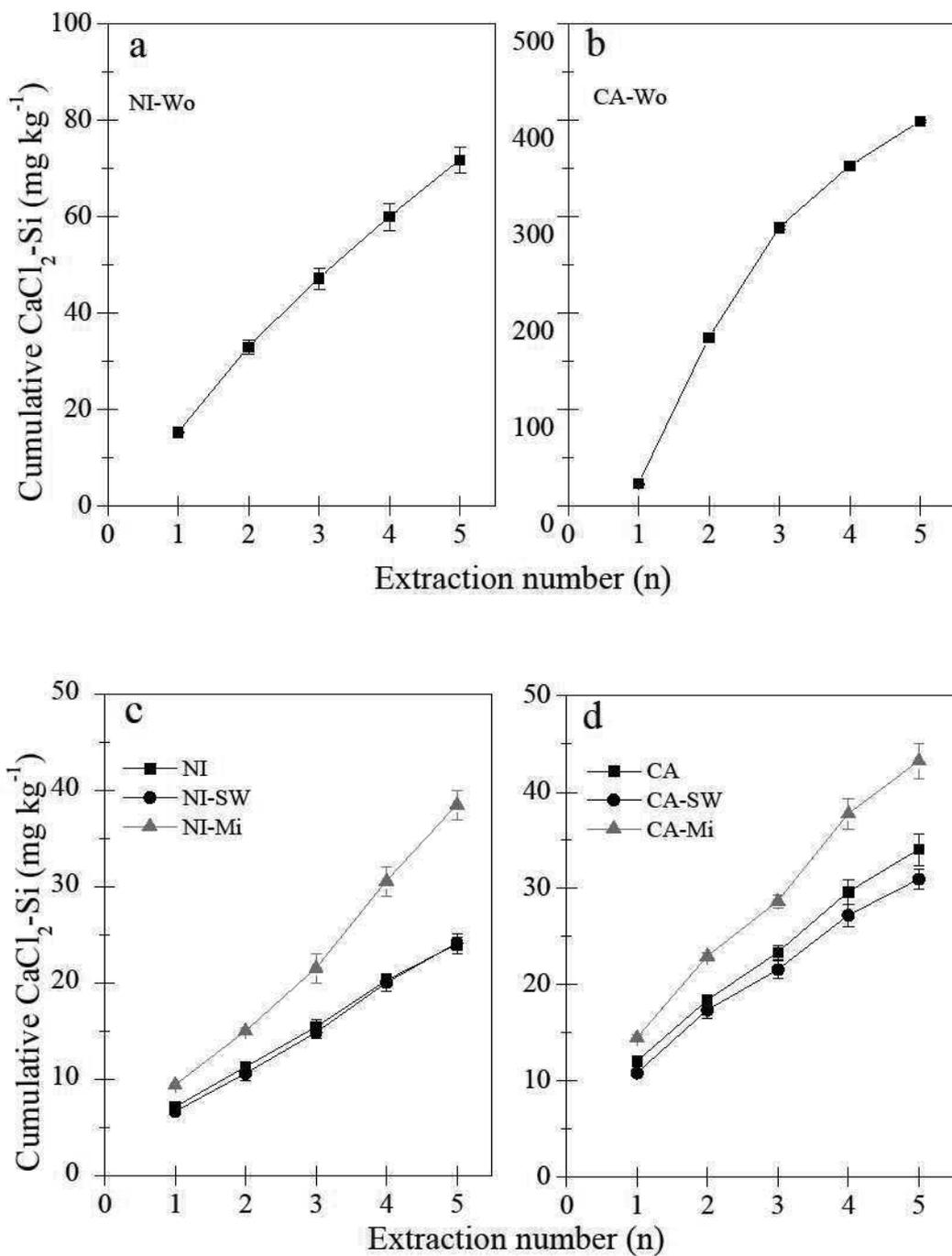


Figure 2. XRD patterns of the clay-size fraction ($<2 \mu\text{m}$) of the Cambisol CA (a) and Nitisol NI (b) after K^+ -saturation at 20, 105, 300 and 550°C; Mg^{2+} -saturation at 20 °C, and saturation with ethylene-glycol.



461

462
 463 **Figure 3.** Plot of the cumulative amount of CaCl₂ extractable Si content against the extraction number (the
 464 Si content at each number is added to the Si contents extracted following the preceding(s)
 465 extraction(s) in (a, b) soil:wollastonite (a, b: NI-Wo and CA-Wo); (c) NI, NI-Mi and NI-SW, and
 466 (d) CA, CA-Mi and CA-SW.
 467

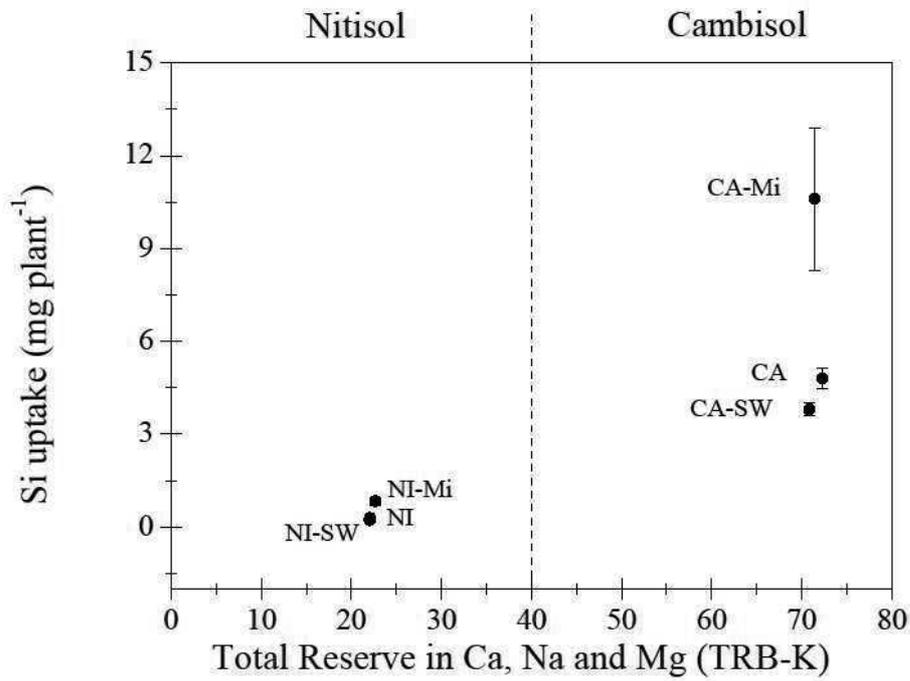


Figure 4. Plot of Si uptake by cotton plants against the total reserve of Ca, Mg and Na minerals (excluding K-bearing muscovite) in the Cambisol (CA) and Nitisol (NI).