



**HAL**  
open science

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

Zimin Li, Bruno Li, Johan Yans, Nicolas Dufour, David Houben,  
Jean-Thomas Cornélis

► **To cite this version:**

Zimin Li, Bruno Li, Johan Yans, Nicolas Dufour, David Houben, et al.. Phytolith-rich biochar increases cotton biomass and silicon-mineralomass in a highly weathered soil. *Journal of Plant Nutrition and Soil Science*, 2018, 181 (4), pp.537-546. 10.1002/jpln.201800031 . hal-02176368

**HAL Id: hal-02176368**

**<https://hal.science/hal-02176368v1>**

Submitted on 8 Jul 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1  
2  
3 1 **Phytolith-rich biochar increases cotton biomass and silicon-mineralomass in a highly**  
4  
5 2 **weathered soil**

6  
7  
8  
9 3 Zimin Li<sup>1\*</sup>, Bruno Delvaux<sup>1</sup>, Johan Yans<sup>2</sup>, Nicolas Dufour<sup>1</sup>, David Houben<sup>3</sup>, Jean-Thomas Cornelis<sup>4</sup>

10  
11  
12 4 <sup>1</sup>Université catholique de Louvain, Earth and Life Institute, soil science, 1348 Louvain-la-Neuve, Belgium

13  
14  
15 5 <sup>2</sup>Department of Geology, NaGRIDD, University of Namur, 5000 Namur, Belgium

16  
17  
18 6 <sup>3</sup>HydrISE, Institut Polytechnique LaSalle Beauvais, rue Pierre Waguet 19, 60026 Beauvais Cedex, France

19  
20  
21 7 <sup>4</sup>BIOSE department, Gembloux Agro-Bio Tech, University of Liege, 5030 Gembloux, Belgium

22  
23  
24 8 **\*Corresponding author:** zimin.li@uclouvain.be (Zimin LI)

25  
26  
27  
28 9 **Address:** Université catholique de Louvain, Earth and Life Institute, soil science, 1348 Louvain-la-Neuve,  
29  
30 10 Belgium, Croix du Sud 2/L7.05.10,1348 Louvain-la-Neuve, Belgium

31  
32  
33 11 Resubmitted to the journal of *Journal of Plant Nutrition and Soil Science (jpln.201700236)*

34  
35  
36 12 **Tables: 4**

37  
38  
39 13 **Figures: 4**

40  
41  
42 14 **Pages: 24**  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 **15 Abstract**  
4  
5

6  
7 16 Non-essential silicon (Si) is beneficial to plants. It increases the biomass of Si-accumulator plants by  
8  
9 17 improving photosynthetic activity and alleviating stresses. Desilication, however, takes place because of  
10  
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.  
14

15  
16 20 Here, we applied two biochar materials differing in Si content on soils differing in weathering stage: a  
17  
18 21 young Cambisol and a highly weathered Nitisol. We studied the impact of biochar supply on the  
19  
20 22 bioavailability of Si, cotton biomass and Si mineralomass. The biochar materials derived from,  
21  
22 23 respectively: *Miscanthus x giganteus* –Mi– (34.6 g Si kg<sup>-1</sup> in biochar) and soft woody material –SW– (0.9  
23  
24 24 g Si kg<sup>-1</sup> in biochar). They were compared to conventional Si fertilizer wollastonite –Wo– (CaSiO<sub>3</sub>).  
25  
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 CaCl<sub>2</sub> extraction.  
29  
30

31  
32 27 In the Cambisol, the proportion [CaCl<sub>2</sub> extractable Si: total Si content] was significantly smaller for Mi  
33  
34 28 (0.9%) than for Wo (5.2%). In the Nitisol, this proportion was much larger for Mi (1.4%) than for Wo  
35  
36 29 (0.7%). Mi-biochar significantly increased Si-mineralomass relatively to SW-biochar in both soils. This  
37  
38 30 increase was, however, much larger in the Nitisol (5.9-fold) than in the Cambisol (2.2-fold).  
39  
40

41  
42 31 Mi biochar is thus an alternative Si fertilizer to Wo to supply bioavailable Si, increase plant biomass, and  
43  
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.  
47  
48

49 34 **Keywords** biochar, bioavailable silicon, soil desilication, cotton  
50  
51 35  
52  
53  
54  
55  
56  
57  
58  
59  
60

## 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 ( $\text{H}_4\text{SiO}_4^0$ ) is ubiquitous in soil solution  
40 where plant roots take it up. In plants, mass flow transports  $\text{H}_4\text{SiO}_4^0$  upwards to transpiration sites.  
41 Therein, water loss increases  $\text{H}_4\text{SiO}_4^0$  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

1  
2  
3 60 oxygen-limited conditions. Pyrolysis converts organic substances into stable C compounds, hence  
4  
5 61 preserves atmospheric C (Lehmann and Joseph, 2015; Lehmann et al., 2011). Applied to soil, biochar  
6  
7 62 retains and supplies plant nutrients (Glaser et al., 2002; Laird et al., 2010; Lehmann et al., 2003), increases  
8  
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  
12  
13 65 density and surface area (Liang et al., 2006). Yet the effect of biochar on plant growth largely depends on  
14  
15 66 soil properties and biochar types (Biederman and Harpole, 2013; Crane-Droesch et al., 2013; Jeffery et  
16  
17 67 al., 2011).

18  
19  
20  
21 68 Pyrolysis of plant residues concentrates PhSi minerals (Houben et al., 2014) which in turn contribute to  
22  
23 69 supply DSi (Houben et al., 2014; Xiao et al., 2014), and increase Si uptake by plants (Liu et al., 2014). The  
24  
25 70 impact of both the PhSi content of biochar and soil silicon availability on plant growth and Si uptake is,  
26  
27 71 however, unknown. Here, we used two biochars differing in Si content, and apply them on soils differing  
28  
29 72 in weathering stage, respectively, a young Cambisol and an old, highly weathered, Nitisol. We studied the  
30  
31 73 release of DSi after biochar application. We further investigated the effect of biochar on soil fertility, plant  
32  
33 74 biomass and Si mineralomass, and compared it to the one of CaSiO<sub>3</sub>-wollastonite.

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

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

41  
42  
43 77 Biochars and wollastonite. The biochars were produced by industrial pyrolysis (550°C, heating rate  
44  
45 78 65 °C/min, kiln residence time 12 min) at UK Biochar Research Centre (UKBRC), respectively from  
46  
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.

52  
53  
54  
55 82 Soils and soil:amendment mixtures. The two soils key out as, respectively, a Dystric Cambisol (CA) and a

1  
2  
3 83 Rhodic Nitisol (NI) in the WRB system (IUSS, 2014). CA (Forest of Lauzelle, Louvain-la Neuve,  
4  
5 84 Belgium) developed from quaternary calcareous silty loess under humid temperate conditions (Titeux and  
6  
7 85 Delvaux, 2009). NI is a paleosol from the quarry of Transinne (Belgium), formed under humid tropical  
8  
9 86 paleo-conditions. The quarry exhibits a deep 65m saprolithic profile derived from Early Devonian  
10  
11 87 bedrock, containing kaolinite, resistant muscovite and quartz, and Fe oxyhydroxides (Thiry et al., 2006).  
12  
13 88 The soil samples were air-dried and sieved at 2-mm. The soil:amendment mixtures were made at 100:3  
14  
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 *CaCl<sub>2</sub> extraction of Si*

20  
21  
22 91 The extraction was carried out on the Si amendments, soils and soil:amendment mixtures before the cotton  
23  
24 92 pot experiment. The CaCl<sub>2</sub>-extractable Si content (CaCl<sub>2</sub>-Si) was determined using a 5g:50ml (0.01 M  
25  
26 93 CaCl<sub>2</sub>) soil:solution ratio, and a 5h continuous shaking time (Haysom and Chapman, 1975). After  
27  
28 94 centrifuged at 3,000×g for 20 min, the supernatant was separated for analysis. The residues were  
29  
30 95 submitted to five successive extractions during 5 days. The concentration of Si was measured in each  
31  
32 96 extract by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

33  
34  
35  
36 97 Analyses. pH was measured in, respectively, H<sub>2</sub>O and KCl 1M, with 5g:25ml suspensions. The CEC and  
37  
38 98 content of exchangeable cations were determined using CH<sub>3</sub>COONH<sub>4</sub> 1M buffered at pH=7 (Chapman,  
39  
40 99 1965). Elemental analysis was carried out after calcination and Li-metaborate + Li-tetraborate fusion  
41  
42 100 (Chao and Sanzalone, 1992). The elemental contents were determined by ICP-AES. Elemental contents of  
43  
44 101 alkaline and alkaline-earth cations were summed up as the total reserve in bases (TRB), which estimates  
45  
46 102 the content of weatherable minerals (Herbillon, 1986). Total carbon (C) and nitrogen (N) contents were  
47  
48 103 measured by dry combustion with a CNS analyzer (Flash EA1112 Series).

49  
50  
51  
52 104 Scanning Electron Microscopy (SEM). The analyses of biochar particles were performed on specimens  
53  
54 105 using a JEOL FEG SEM 7600F, equipped with Energy Dispersive X-ray Spectrometry system (EDX, Jeol

1  
2  
3 106 JSM2300 with a resolution < 129 eV) operating at 15 keV with a working distance of 8 mm for the  
4  
5 107 element detection. The acquisition time for the chemical spectra lasted 100 s with a probe current of 1 nA.  
6  
7

### 8 ***Plant material and analyses, pot experiment*** 9

10  
11  
12 109 Cotton plant. We used *Gossypium hirsutum*, var (STAM 59A-Bollgard II) from southern Burkina Faso.  
13

14  
15 110 Pot experiment in a phytotron (5 months). The soil:amendment mixtures (100:3 g:g) were irrigated with  
16  
17 111 deionized water and allowed to equilibrate for a week at 70% of field water holding capacity before  
18  
19 112 planting. After germination in deionized water, the plantlets were allowed to grow up to 5-cm. They were  
20  
21 113 then transplanted into pots (7.5 L) containing the respective soil:amendment mixtures (3kg dry weight), in  
22  
23 114 triplicate under 28°C and relative humidity at 80%. Each pot was watered every three days with 33 ml  
24  
25 115 deionized water during the first two months, and 100 ml the last three months. No nutrients were supplied.  
26  
27 116 We collected the aboveground plant part after 5 months for further drying at 55°C during 7 days prior to  
28  
29 117 biomass weighing.  
30  
31

32  
33 118 Analyses. Mineral analysis was carried out after calcination at 450°C for 1 day and fusion in Li-  
34  
35 119 metaborate + Li-tetraborate at 1,000°C (Chao and Sanzalone, 1992), followed by ash dissolution with  
36  
37 120 concentrated HNO<sub>3</sub>. Element contents were measured by ICP-AES. Element mineralomass was computed  
38  
39 121 from total element contents and cotton biomass.  
40  
41

### 42 ***Statistical analyses*** 43

44  
45  
46 123 We used the SPSS 17.0 statistical software to carry out the one-way analysis of variance (ANOVA) (at  
47  
48 124  $p < 0.05$  level) and LSD (at  $p < 0.05$  level).  
49  
50

## 51 **Results** 52

53  
54  
55 126 *Properties of the biochars and wollastonite*  
56  
57  
58  
59  
60

1  
2  
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  
4  
5 128 (%) was 1.2 in SW and 2.0 in Mi. The contents of  $\text{CaCl}_2$  extractable Si ( $\text{g kg}^{-1}$ ) were larger in Mi (11.4)  
6  
7 129 than in Wo (8.8) and SW (0.01). Si content of Wo amounted to  $233.3 \text{ g kg}^{-1}$  which was 7 times larger than  
8  
9 130 that of Mi ( $34.6 \text{ g kg}^{-1}$ ), and 259 times larger than in SW ( $0.9 \text{ g kg}^{-1}$ ). The contents of Ca, Mg in Wo were  
10  
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  
12  
13 132 in SW (2.6) and Wo (1.1). Figure 1 illustrated the SEM micrographs and associated EDX spectra of  
14  
15 133 biochar materials SW and Mi. In particular, Fig. 1(f) showed the occurrence of dumbbell-shaped, fine silt-  
16  
17 134 sized phytoliths in Mi biochar. As inferred from Fig.1 (e), they were abundant and undamaged after  
18  
19 135 pyrolysis at  $550 \text{ }^\circ\text{C}$ .

### 23 136 *Soil and soil:amendment properties*

24  
25  
26 137 CA and NI are acid soils since their  $\text{pH}_{\text{water}}$  values were 4.6 and 5.2, respectively (Table 2). C and N  
27  
28 138 contents, CEC and contents of exchangeable cations were larger in CA than in NI. Of course, biochar  
29  
30 139 application resulted in a huge increase in C content while Wo did not. The latter application led to a  
31  
32 140 marked increase in pH and content of exchangeable Ca. SW application did not generate any change of  
33  
34 141 pH, CEC, contents of exchangeable cations and base saturation whatever the soil type. To the contrary, Mi  
35  
36 142 application induced a significant increase of these parameters. In particular, exchangeable K content  
37  
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  
39  
40 144 Al and Fe ( $\text{g kg}^{-1}$ ) amounted to, respectively, 39.2 and 18.5 in CA, 96.5 and 30.6 in NI (Table 3). Total Si  
41  
42 145 content ( $\text{g kg}^{-1}$ ) in CA and NI was 376.8 and 311.9, respectively. Computed values of  $\text{Si}/(\text{Al}+\text{Fe})$  atomic  
43  
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.  
45  
46 147 Residual weatherable minerals in CA were plagioclase and feldspar, and soil clay minerals. From Figure 2,  
47  
48 148 CA clay minerals consisted of kaolinite and an assemblage of 2:1:1 and 2:1 clay minerals involving  
49  
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  
53  
54 151 occurrence of muscovite, a dioctahedral mica resistant to weathering. The large amount of non-  
55  
56  
57  
58  
59  
60



1  
2  
3 152 exchangeable K (Table 3) thus hid the advanced weathering stage of NI because muscovite is stable and  
4  
5 153 does not weather in soils. The reserve of weatherable minerals was then estimated by the difference  
6  
7 154 between TRB and the content of non-exchangeable K, excluding K-bearing muscovite. [TRB-K] (cmol<sub>c</sub>  
8  
9 155 kg<sup>-1</sup>) amounted to 72.5 in CA and 22.1 in NI, indicating the strongly advanced weathering stage of NI.  
10  
11 156 [TRB-K] did not increase following biochar application. To the contrary, wollastonite application  
12  
13 157 generated a marked increase of total Ca content (cmol<sub>c</sub> kg<sup>-1</sup>): from 15 to 63 in CA, and from 1 to 48 in NI.  
14  
15 158 Cumulative CaCl<sub>2</sub>-Si (mg kg<sup>-1</sup>) (Table 3, Figure 3) was significantly larger in CA (34) than in NI (24).  
16  
17 159 CaCl<sub>2</sub>-Si significantly ( $p < 0.01$ ) increased after Wo application in CA (398.7) and NI (71.7). Unlike SW,  
18  
19 160 Mi significantly ( $p < 0.01$ ) increased CaCl<sub>2</sub>-Si in CA (43.2) and NI (38.5).  
20  
21  
22

### 23 161 *Biomass and mineralomass of cotton plants*

24  
25  
26 162 The cotton biomass (g plant<sup>-1</sup>) 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<sup>-1</sup>) 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  
33  
34 166 kg<sup>-1</sup> DW): 0.65 for CA-Mi and 0.74 for NI-Mi, as well as plant Si mineralomass (mg Si plant<sup>-1</sup>): 10.52 for  
35  
36 167 CA-Mi and 1.12 for NI-Mi). Si mineralomass indeed increased by 120% in CA-Mi and 180% in NI-Mi  
37  
38 168 relatively to the untreated soils CA and Mi.  
39  
40  
41

## 42 169 **Discussion**

### 43 44 45 46 170 *Weathering stage of soils*

47  
48  
49 171 The values of TRB and Si/(Al+Fe) ratio as well as the nature of secondary clay minerals are used to  
50  
51 172 assess soil weathering stage (*Herbillon, 1986*). Taking into account the stability of muscovite in soils, NI  
52  
53 173 exhibited an advanced weathering stage characteristic of strongly weathered ferrallitic soils (*Herbillon,*  
54  
55 174 1986). In CA, the large dominance of quartz is characteristic of soils of the Belgian loess belt, in which the  
56  
57  
58  
59  
60

1  
2  
3 175 reserve of weatherable minerals is concentrated in the clay fraction (*Brahy et al., 2000*). CA soil clay  
4  
5 176 minerals (kaolinite, chlorite, illite, vermiculite and smectite: Figure 2a) revealed a mineralogical  
6  
7 177 assemblage typical of moderately weathered soils under temperate climates. To the contrary, NI soil clay  
8  
9 178 minerals (Figure 2b) make an assemblage typical for desilicated, highly weathered soils formed under  
10  
11 179 humid tropical conditions. Consequently, CaCl<sub>2</sub>-Si content was significantly larger in CA than in NI  
12  
13  
14 180 (Figure 3).

15  
16  
17 181 *Mobility of Si in soil: amendment mixtures*

18  
19  
20 182 As it is linked to the DSi pool from which plant roots take up Si, CaCl<sub>2</sub>-Si could quantify the pool of  
21  
22 183 bioavailable Si in soils (*Sauer et al., 2006*). Cumulative CaCl<sub>2</sub>-Si (mg kg<sup>-1</sup>) 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  
25  
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, CaCl<sub>2</sub>-Si was systematically smaller in NI:amendment mixtures. Part of H<sub>4</sub>SiO<sub>4</sub><sup>o</sup>  
29  
30 187 released by amendments was undoubtedly adsorbed by oxide surfaces in NI as it commonly occurs in  
31  
32 188 highly weathered soils (*Herbillon et al., 1977*).

33  
34  
35  
36 189 To further assess Si mobility, we define the efficiency of each amendment (AM) using CaCl<sub>2</sub>-Si and total  
37  
38 190 Si contents (Table 3) as follows:

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

39  
40  
41  
42  
43  
44  
45  
46 191 In CA, the efficiency of MI was significantly smaller (0.9%) than that of Wo (5.2%). To the contrary, in  
47  
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<sup>-1</sup>, Table 1) and  
53  
54 195 the accessibility of phytoliths in Mi (Figure 1 e, f) support that phytoliths readily contribute to DSi. They  
55  
56  
57  
58  
59  
60

1  
2  
3 196 resist to pyrolytic temperatures as high as 550°C, and further dissolve to release DSi given their solubility  
4  
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).  
12  
13

14  
15 201 The release of bioavailable Si in Mi-amended soils was not affected by soil type and weathering stage.  
16  
17 202 The biochar derived from high-Si accumulator *Miscanthus* is thus an alternative Si fertilizer to  
18  
19 203 wollastonite to supply bioavailable Si in the highly weathered Nitisol.  
20  
21

#### 22 204 *Effect of biochar amendment on soil properties*

23  
24

25 205 As already reported (*Sohi et al.*, 2010; *Van Zwieten et al.*, 2010), biochar application to soils affects their  
26  
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  
32  
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.  
36  
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;  
42  
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  
46  
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.*  
52  
53 219 (2006) for black C. The larger BS after Mi amendment was due to the larger nutrient content (Ca, Mg and  
54  
55  
56  
57  
58  
59  
60

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 ( $\text{g plant}^{-1}$ ): 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 ( $\text{g.plant}^{-1}$ ) (0.2 – 1.5

1  
2  
3 243 g.plant<sup>-1</sup>) was very low in NI (0.2–1.5) compared to CA (8.8–16.2) (Table 4). As discussed above,  
4  
5 244 phytoliths were abundant in Mi; they dissolved and released DSi, thereby contributing to the pool of  
6  
7 245 bioavailable Si, which was readily taken up by plant roots (Figure 1, 2, 3; Table 3). This effect was  
8  
9 246 particularly important in the highly weathered Nitisol depleted in primary and secondary silicates.  
10  
11

## 12 247 **Conclusion**

13  
14  
15  
16 248 *Miscanthus* biochar and wollastonite amendments significantly ( $p < 0.01$ ) enhanced the release of CaCl<sub>2</sub>-  
17  
18 249 extractable Si in a young Cambisol and an old, highly weathered Nitisol. Soft wood biochar amendment  
19  
20 250 had no effect on the release of CaCl<sub>2</sub>-extractable Si in both soils. *Miscanthus* biochar supply increased  
21  
22 251 ECEC, particularly the content of exchangeable K, while soft wood biochar did not have any effect on  
23  
24 252 these parameters whatever the soil type. Both biochar amendments induced a significant effect on C and N  
25  
26 253 contents in both soils. *Miscanthus* biochar generated a significant increase of cotton biomass. That  
27  
28 254 increase was, however, larger in the Nitisol than in the Cambisol, since it was 4.7-fold in the former and  
29  
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  
31  
32 256 much larger than in the Cambisol (2.2-fold), supporting a larger efficiency of Si release from *Miscanthus*  
33  
34 257 phytoliths in the Nitisol.  
35  
36  
37

38 258 Our data thus highlight that *Miscanthus* biochar is an alternative Si amendment to wollastonite to supply  
39  
40 259 bio-available Si, increase plant biomass and promote the biological cycle of Si in the soil-plant system.  
41  
42 260 This positive impact of a Si-rich biochar is, however, larger in the old, desilicated, highly weathered  
43  
44 261 Nitisol. Overall, it demonstrates that Si is progressively released from phytolith-rich biochar, and directly  
45  
46 262 contributes to the pool of bioavailable Si for plant root uptake in soil. This is particularly important for  
47  
48 263 agro-ecosystems in which high-Si accumulator plants grow in highly weathered, desilicated soils. Further  
49  
50 264 field experiments are required to confirm the effect of phytolith-rich biochar as a Si fertilizer over the  
51  
52 265 whole plant cycle. Furthermore, the efficiency of various biochar types to release Si and plant nutrients  
53  
54  
55 266 should be studied.  
56  
57  
58  
59  
60

## 267 Acknowledgements

268 We thank A. Iserentant and C. Givron for laboratory assistance (UCL). Z Li is supported by the “Fonds  
 269 Spécial de Recherché” of the UCL in 2014-2015 and the Aspirant (ASP)-Fonds National de la Recherché  
 270 Scientifique» (FNRS) of Belgium in 2015-2019.

## 271 References

- 272 *Alexandre, A. , Bouvet, M. , Abbadie, L. (2011). The role of savannas in the terrestrial Si cycle: a case-*  
 273 *study from Lamto, Ivory Coast. *Global and Planetary Change* 78, 162-169.*
- 274 *Barão, L. , Clymans, W. , Vandevenne, F. , Meire, P. , Conley, D., Struyf, E. (2014). Pedogenic and*  
 275 *biogenic alkaline-extracted silicon distributions along a temperate land-use gradient. *European**  
 276 *Journal of Soil Science* 65, 693-705.
- 277 *Belanger, R. R. (1995). Soluble silicon: its role in crop and disease management of greenhouse crops.*  
 278 *Plant Dis* 79, 329-336.
- 279 *Berthelsen, S. , Noble, A. , Garside, A. (2001). Silicon research down under: past, present, and future.*  
 280 *Studies in Plant Science* 8, 241-255.
- 281 *Biederman, L. A. , Harpole, W. S. (2013). Biochar and its effects on plant productivity and nutrient*  
 282 *cycling: a meta-analysis. *GCB bioenergy* 5, 202-214.*
- 283 *Blecker, S. W. , McCulley, R. L. , Chadwick, O. A. , Kelly, E. F. (2006). Biologic cycling of silica across a*  
 284 *grassland bioclimate sequence. *Global Biogeochemical Cycles* 20.*
- 285 *Brahy, V. , Deckers, J. , Delvaux, B. (2000). Estimation of soil weathering stage and acid neutralizing*  
 286 *capacity in a toposequence Luvisol–Cambisol on loess under deciduous forest in Belgium.*  
 287 *European Journal of Soil Science* 51, 1-13.
- 288 *Chao, T. , Sanzolone, R. (1992). Decomposition techniques. *Journal of Geochemical Exploration* 44, 65-*  
 289 *106.*
- 290 *Chapman, H. (1965). Cation-exchange capacity. Methods of soil analysis. Part 2. *Chemical and**  
 291 *microbiological properties*, 891-901.
- 292 *Clarholm, M. (1994). Granulated wood ash and a ‘N-free’ fertilizer to a forest soil—effects on P*  
 293 *availability. *Forest Ecology and Management* 66, 127-136.*
- 294 *Cornelis, J.-T. , Titeux, H. , Ranger, J. , Delvaux, B. (2011). Identification and distribution of the readily*  
 295 *soluble silicon pool in a temperate forest soil below three distinct tree species. *Plant and soil* 342,*  
 296 *369-378.*
- 297 *Cornelis, J. T. , Delvaux, B. (2016). Soil processes drive the biological silicon feedback loop. *Functional**  
 298 *Ecology* 30, 1298-1310.
- 299 *Crane-Droesch, A. , Abiven, S. , Jeffery, S., Torn, M. S. (2013). Heterogeneous global crop yield response*  
 300 *to biochar: a meta-regression analysis. *Environmental Research Letters* 8, 044049.*
- 301 *Datnoff, L. E. , Heckman, J. R. (2014). Silicon fertilizers for plant disease protection. In "World Fertilizer*  
 302 *Congress", Vol. 16, pp. 36.*
- 303 *Epstein, E. (1994). The anomaly of silicon in plant biology. *Proceedings of the National Academy of**  
 304 *Sciences* 91, 11-17.
- 305 *Fauteux, F. , Rémus-Borel, W. , Menzies, J. G. , Bélanger, R. R. (2005). Silicon and plant disease*  
 306 *resistance against pathogenic fungi. *FEMS Microbiology letters* 249, 1-6.*
- 307 *Fraysse, F. , Pokrovsky, O. S., Schott, J. , Meunier, J.-D. (2006). Surface properties, solubility and*  
 308 *dissolution kinetics of bamboo phytoliths. *Geochimica et Cosmochimica Acta* 70, 1939-1951.*
- 309 *Fraysse, F. , Pokrovsky, O. S., Schott, J. , Meunier, J.-D. (2009). Surface chemistry and reactivity of plant*

- 1  
2  
3 310 phytoliths in aqueous solutions. *Chemical Geology* **258**, 197-206.
- 4 311 Gérard, F., Mayer, K., Hodson, M., Ranger, J. (2008). Modelling the biogeochemical cycle of silicon in  
5 312 soils: application to a temperate forest ecosystem. *Geochimica et Cosmochimica Acta* **72**, 741-  
6 313 758.
- 7 314 Glaser, B., Lehmann, J., Zech, W. (2002). Ameliorating physical and chemical properties of highly  
8 315 weathered soils in the tropics with charcoal—a review. *Biology and fertility of soils* **35**, 219-230.
- 9 316 Haynes, R. J. (2014). A contemporary overview of silicon availability in agricultural soils. *Journal of*  
10 317 *Plant Nutrition and Soil Science* **177**, 831-844.
- 11 318 Haynes, R. J., Belyaeva, O., Kingston, G. (2013). Evaluation of industrial wastes as sources of fertilizer  
12 319 silicon using chemical extractions and plant uptake. *Journal of Plant Nutrition and Soil Science*  
13 320 **176**, 238-248.
- 14 321 Haysom, M., Chapman, L. (1975). Some aspects of the calcium silicate trials at Mackay. In  
15 322 "Proceedings".
- 16 323 Henriot, C., Bodarwé, L., Dorel, M., Draye, X., Delvaux, B. (2008). Leaf silicon content in banana (*Musa*  
17 324 spp.) reveals the weathering stage of volcanic ash soils in Guadeloupe. *Plant and Soil* **313**, 71-82.
- 18 325 Herbillon, A. (1986). Chemical estimation of weatherable minerals present in the diagnostic horizons of  
19 326 low activity clay soils. In "Proceedings of the 8th International Clay Classification Workshop:  
20 327 Classification, Characterization and Utilization of Oxisols (part 1)[Beinroth, FH, Camargo, MN  
21 328 and Eswaran (ed.)][39–48](Rio de Janeiro, 1986)".
- 22 329 Herbillon A., Gallez A., Juo S.R. (1977) Characteristics of Silica Sorption and Solubility as Parameters to  
23 330 Evaluate the Surface Properties of Tropical Soils: II. The Index of Silica Saturation. *Soil Science*  
24 331 *Society of America Journal* **41**, 1151-1154.
- 25 332 Houben, D., Sonnet, P., Cornelis, J.-T. (2014). Biochar from *Miscanthus*: a potential silicon fertilizer.  
26 333 *Plant and soil* **374**, 871-882.
- 27 334 Issaharou-Matchi, I., Barboni, D., Meunier, J.-D., Saadou, M., Dussouillez, P., Contoux, C., Zirihi-  
28 335 Guede, N. (2016). Intraspecific biogenic silica variations in the grass species *Pennisetum*  
29 336 *pedicellatum* along an evapotranspiration gradient in South Niger. *Flora-Morphology,*  
30 337 *Distribution, Functional Ecology of Plants* **220**, 84-93.
- 31 338 IUSS (2014). World reference base for soil resources 2014 international soil classification system for  
32 339 naming soils and creating legends for soil maps. *FAO*, Rome.
- 33 340 Jeffery, S., Verheijen, F. G., Van Der Velde, M., Bastos, A. C. (2011). A quantitative review of the effects  
34 341 of biochar application to soils on crop productivity using meta-analysis. *Agriculture, ecosystems*  
35 342 *& environment* **144**, 175-187.
- 36 343 Jones, L., Handreck, K. (1963). Effects of iron and aluminium oxides on silica in solution in soils.
- 37 344 Jones, L., Handreck, K. (1967). Silica in soils, plants, and animals. *Advances in agronomy* **19**, 107-149.
- 38 345 Keller, C., Guntzer, F., Barboni, D., Labreuche, J., Meunier, J.-D. (2012). Impact of agriculture on the  
39 346 Si biogeochemical cycle: input from phytolith studies. *Comptes Rendus Geoscience* **344**, 739-746.
- 40 347 Kloss, S., Zehetner, F., Wimmer, B., Buecker, J., Rempt, F., Soja, G. (2014). Biochar application to  
41 348 temperate soils: effects on soil fertility and crop growth under greenhouse conditions. *Journal of*  
42 349 *plant nutrition and soil science* **177**, 3-15.
- 43 350 Laird, D. A., Fleming, P., Davis, D. D., Horton, R., Wang, B., Karlen, D. L. (2010). Impact of biochar  
44 351 amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* **158**, 443-449.
- 45 352 Lehmann, J., da Silva Jr, J. P., Steiner, C., Nehls, T., Zech, W., Glaser, B. (2003). Nutrient availability  
46 353 and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin:  
47 354 fertilizer, manure and charcoal amendments. *Plant and soil* **249**, 343-357.
- 48 355 Lehmann, J., Joseph, S. (2015). "Biochar for environmental management: science, technology and  
49 356 implementation," Routledge.
- 50 357 Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C., Crowley, D. (2011). Biochar  
51 358 effects on soil biota—a review. *Soil Biology and Biochemistry* **43**, 1812-1836.
- 52 359 Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J., Thies, J.,  
53 360 Luizao, F., Petersen, J. (2006). Black carbon increases cation exchange capacity in soils. *Soil*

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 361 *Science Society of America Journal* **70**, 1719-1730.
- 362 Liang, Y. , Sun, W. , Zhu, Y.-G. , Christie, P. (2007). Mechanisms of silicon-mediated alleviation of abiotic  
363 stresses in higher plants: a review. *Environmental pollution* **147**, 422-428.
- 364 Liu, X. , Li, L., Bian, R. , Chen, D. , Qu, J. , Wanjiru Kibue, G. , Pan, G. , Zhang, X. , Zheng, J. , Zheng, J.  
365 (2014). Effect of biochar amendment on soil-silicon availability and rice uptake. *Journal of plant  
366 nutrition and soil science* **177**, 91-96.
- 367 Liu, X. , Zhang, A. , Ji, C., Joseph, S. , Bian, R. , Li, L. , Pan, G. , Paz-Ferreiro, J. (2013). Biochar's effect  
368 on crop productivity and the dependence on experimental conditions—a meta-analysis of  
369 literature data. *Plant and soil* **373**, 583-594.
- 370 Ma, J. F. , Tamai, K. , Yamaji, N. , Mitani, N. , Konishi, S. , Katsuhara, M. , Ishiguro, M. , Murata, Y. ,  
371 Yano, M. (2006). A silicon transporter in rice. *Nature* **440**, 688-691.
- 372 Mahmood, S. , Finlay, R. D. , Fransson, A.-M. , Wallander, H. (2003). Effects of hardened wood ash on  
373 microbial activity, plant growth and nutrient uptake by ectomycorrhizal spruce seedlings. *FEMS  
374 Microbiology Ecology* **43**, 121-131.
- 375 Major, J. , Rondon, M. , Molina, D. , Riha, S. J. , Lehmann, J. (2010). Maize yield and nutrition during 4  
376 years after biochar application to a Colombian savanna oxisol. *Plant and soil* **333**, 117-128.
- 377 McKeague, J. , Cline, M. (1963). Silica in soil solutions: II. The adsorption of monosilicic acid by soil and  
378 by other substances. *Canadian Journal of Soil Science* **43**, 83-96.
- 379 Rajkovich, S. , Enders, A. , Hanley, K. , Hyland, C. , Zimmerman, A. R. , Lehmann, J. (2012). Corn growth  
380 and nitrogen nutrition after additions of biochars with varying properties to a temperate soil.  
381 *Biology and Fertility of Soils* **48**, 271-284.
- 382 Rondon, M. A. , Lehmann, J. , Ramirez, J. , Hurtado, M. (2007). Biological nitrogen fixation by common  
383 beans (*Phaseolus vulgaris* L.) increases with bio-char additions. *Biology and fertility of soils* **43**,  
384 699-708.
- 385 Sauer, D., Saccone, L. , Conley, D. J. , Herrmann, L. , Sommer, M. (2006). Review of methodologies for  
386 extracting plant-available and amorphous Si from soils and aquatic sediments. *Biogeochemistry*  
387 **80**, 89-108.
- 388 Sohi, S. , Krull, E. , Lopez-Capel, E., Bol, R. (2010). A review of biochar and its use and function in soil.  
389 *Advances in agronomy* **105**, 47-82.
- 390 Spokas, K. , Reicosky, D. (2009). Impacts of Sixteen Different Biochars on Soil Greenhouse Gas  
391 Production. *Annals of Environmental Science* **3**, 179-193.
- 392 Struyf, E. , Smis, A. , Van Damme, S. , Garnier, J. , Govers, G. , Van Wesemael, B. , Conley, D. J. ,  
393 Batelaan, O. , Frot, E. , Clymans, W. (2010). Historical land use change has lowered terrestrial  
394 silica mobilization. *Nature communications* **1**, 129.
- 395 Thiry, M. , Quesnel, F. , Yans, J. , Wyns, R. , Vergari, A. , Theveniaut, H. , Simon-Coinçon, R. , Ricordel,  
396 C. , Moreau, M.-G. , Giot, D. (2006). Continental France and Belgium during the early  
397 Cretaceous: paleoweatherings and paleolandforms. *Bulletin de la Société géologique de France*  
398 **177**, 155-175.
- 399 Titeux, H. , Delvaux, B. (2009). Experimental study of DOC, nutrients and metals release from forest  
400 floors developed under beech (*Fagus sylvatica* L.) on a Cambisol and a Podzol. *Geoderma* **148**,  
401 291-298.
- 402 Topoliantz, S. , Ponge, J.-F. , Ballof, S. (2005). Manioc peel and charcoal: a potential organic amendment  
403 for sustainable soil fertility in the tropics. *Biology and Fertility of Soils* **41**, 15-21.
- 404 Van Zwieten, L. , Kimber, S. , Morris, S. , Chan, K. , Downie, A. , Rust, J. , Joseph, S. , Cowie, A. (2010).  
405 Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil  
406 fertility. *Plant and soil* **327**, 235-246.
- 407 Vandevenne, F. , Barão, L. , Ronchi, B. , Govers, G. , Meire, P. , Kelly, E. , Struyf, E. (2015). Silicon pools  
408 in human impacted soils of temperate zones. *Global Biogeochemical Cycles* **29**, 1439-1450.
- 409 Vandevenne, F. , Struyf, E. , Clymans, W. , Meire, P. (2012). Agricultural silica harvest: have humans  
410 created a new loop in the global silica cycle? *Frontiers in Ecology and the Environment* **10**, 243-  
411 248.



- 1  
2  
3 412 *White, A. F. , Vivit, D. V. , Schulz, M. S., Bullen, T. D. , Evett, R. R. , Aagarwal, J.* (2012). Biogenic and  
4 413 pedogenic controls on Si distributions and cycling in grasslands of the Santa Cruz soil  
5 414 chronosequence, California. *Geochimica et Cosmochimica Acta* **94**, 72-94.  
6 415 *Xiao, X. , Chen, B. , Zhu, L.* (2014). Transformation, morphology, and dissolution of silicon and carbon in  
7 416 rice straw-derived biochars under different pyrolytic temperatures. *Environmental science &*  
8 417 *technology* **48**, 3411-3419.  
9 418 *Yamato, M. , Okimori, Y. , Wibowo, I. F. , Anshori, S. , Ogawa, M.* (2006). Effects of the application of  
10 419 charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical  
11 420 properties in South Sumatra, Indonesia. *Soil science and plant nutrition* **52**, 489-495.  
12 421  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 422 **Table1.** Selected properties of the soft wood (SW), *Miscanthus* (Mi) biochars and wollastonite (Wo):  
4 423 pH<sub>water</sub>, total contents of Carbon (C), Nitrogen (N), CaCl<sub>2</sub> extractable Si (CaCl<sub>2</sub>-Si), major  
5 424 alkaline and alkaline-earth cations (Ca, Mg, K, Na), and silicon (Si).  
6

Amendments	pH	<sup>§</sup> C	<sup>§</sup> N	CaCl <sub>2</sub> -Si	Ca	Mg	Na	K	Si
	H <sub>2</sub> O	(%)		g kg <sup>-1</sup>			(g kg <sup>-1</sup> )		
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)

14 425 **Note:** nd means not determined; §: Single measurements only.  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

**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 <sup>-1</sup>	N	CEC	Exchangeable cations (cmol <sub>c</sub> kg <sup>-1</sup> )				BS (%)
	H <sub>2</sub> O	KCl				Ca <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	
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 <sub>2</sub> -Si <sup>1</sup> (mg kg <sup>-1</sup> )	Total Si (g kg <sup>-1</sup> )	Total elements (cmol <sub>c</sub> kg <sup>-1</sup> )				TRB <sup>2</sup>	[TRB-K] <sup>3</sup>	Total elements (g kg <sup>-1</sup> )		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

<sup>1</sup>: cumulative amount after 5 extractions (see also Figure 3);

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

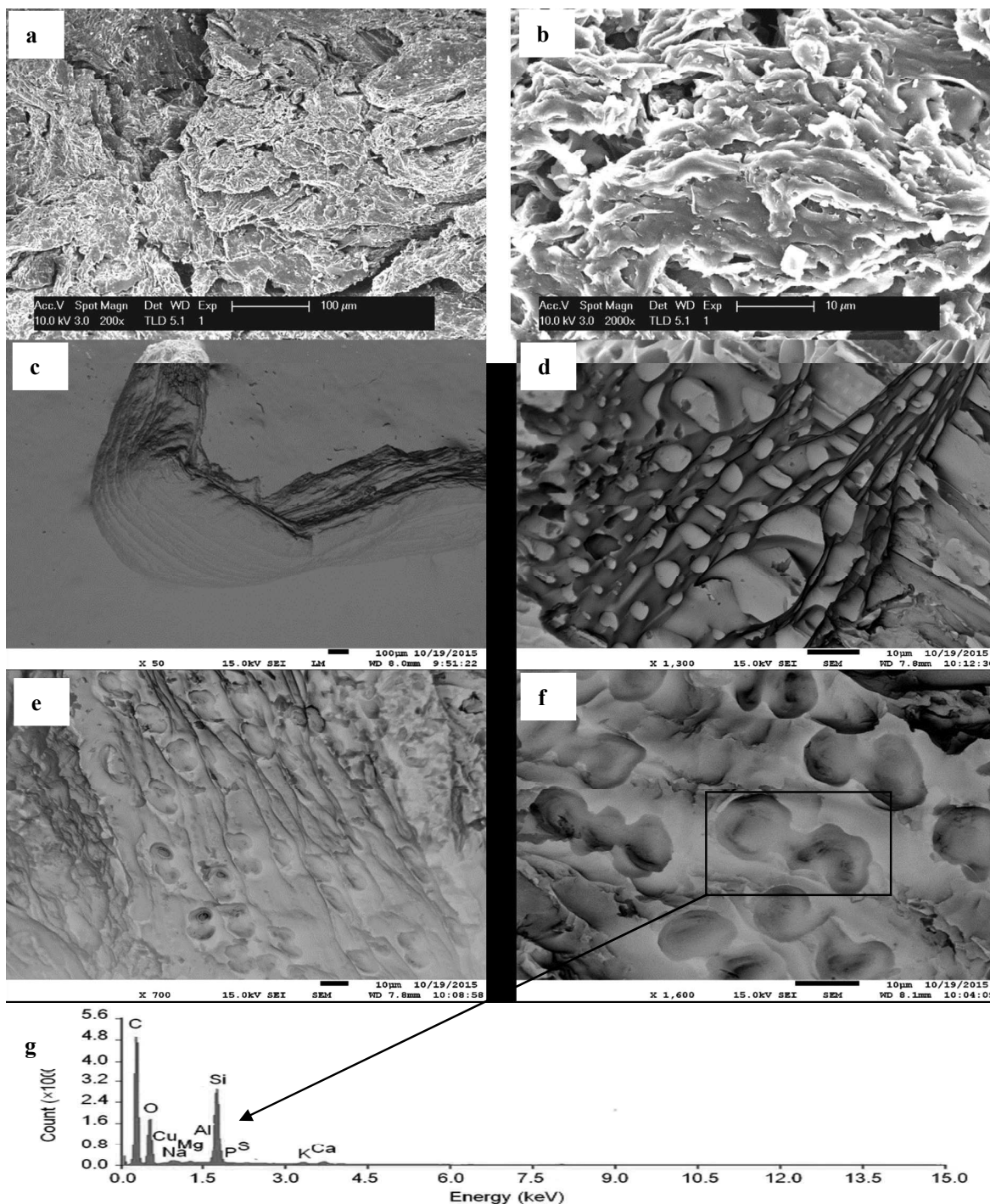
<sup>3</sup>: TRB-K is the sum of total contents of Ca, Mg and Na in soil, excluding non-exchangeable K [total K – exchangeable K], associated with resistant muscovite or oxidized biotite, both dioctahedral micaceous minerals.

**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.

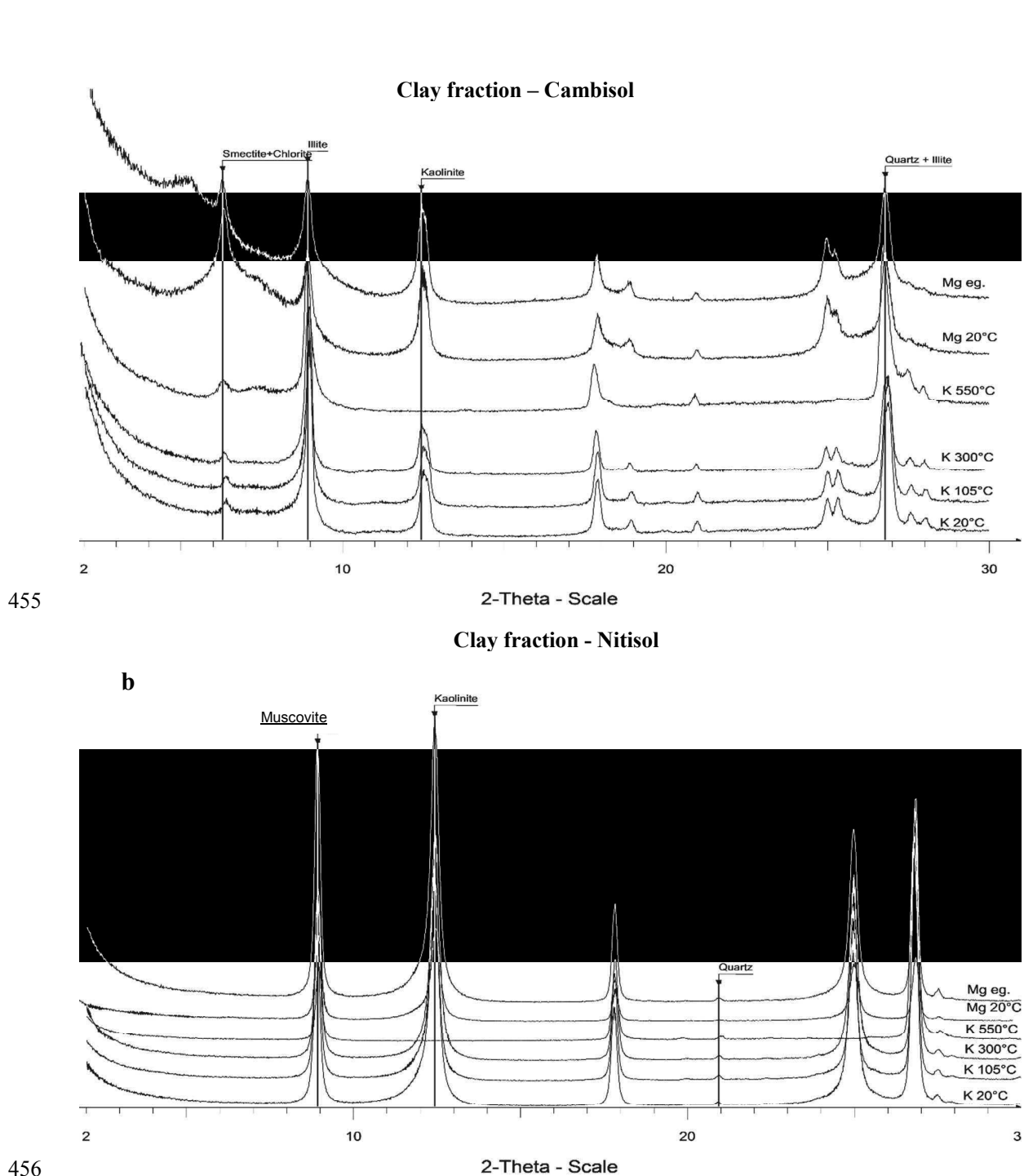
Treatments		CA	CA-SW	CA-Mi	NI	NI-SW	NI-Mi
Biomass	g plant <sup>-1</sup>	8.82(1.10)b	8.63(2.51)b	16.24(2.11)a	0.32(0.07)y	0.24(0.11)y	1.51(0.40)x
Ca	g kg <sup>-1</sup>	14.64(4.59)a	7.79(0.62)b	13.22(2.05)a	3.16(1.09)y	3.82(1.39)y	11.42(2.46)x
Mg		2.76(0.48)a	2.13(0.30)b	2.48(0.27)a	1.54(0.00)y	1.30(0.10)y	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 <sup>-1</sup>	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

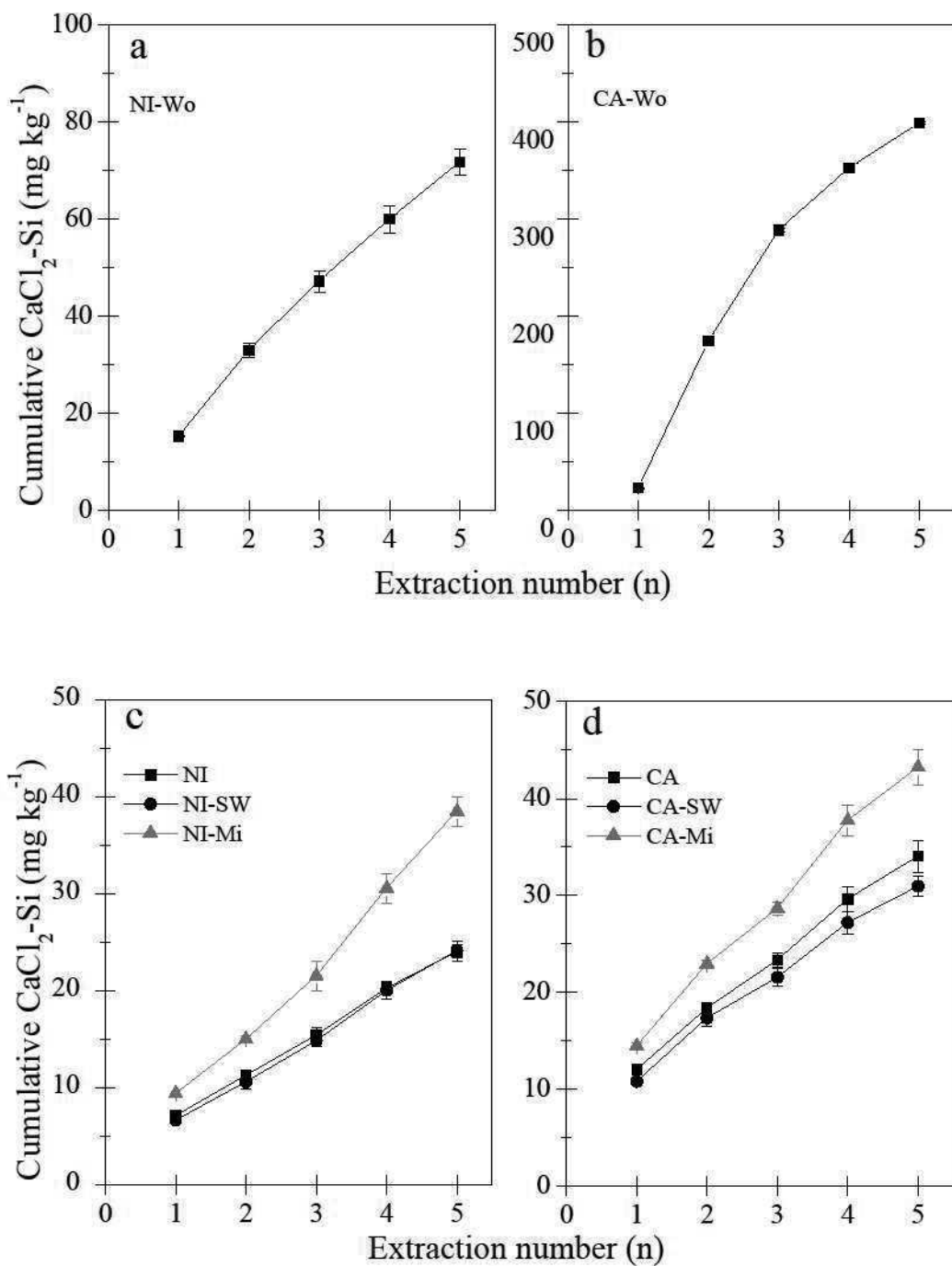
445 **Figures**



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 (SiO<sub>2</sub>·nH<sub>2</sub>O).  
 453  
 454



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

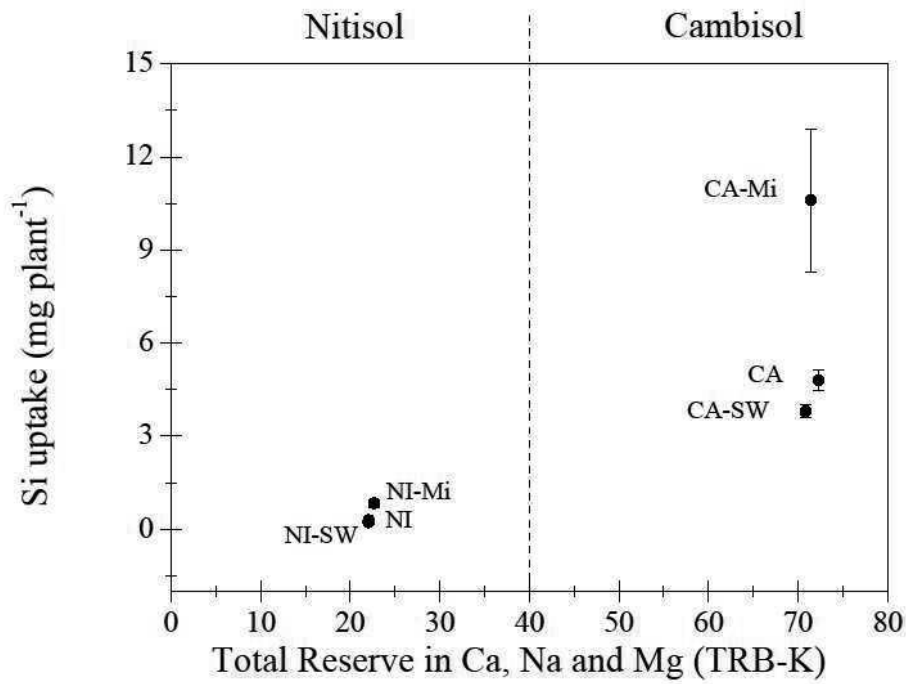


461

462  
 463  
 464  
 465  
 466  
 467

**Figure 3.** Plot of the cumulative amount of  $\text{CaCl}_2$  extractable Si content against the extraction number (the Si content at each number is added to the Si contents extracted following the preceding(s) extraction(s) in (a, b) soil:wollastonite (a, b: NI-Wo and CA-Wo); (c) NI, NI-Mi and NI-SW, and (d) CA, CA-Mi and CA-SW.





**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).