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

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Abstract

Non-essential silicon (Si) is beneficial to plants. It increases the biomass of Si-accumulator plants by improving photosynthetic activity and alleviating stresses. Desilication, however, takes place because of natural soil weathering and removal of harvested biomass. Pyrolysis transforms Si-rich biomass into biochar that can be used to supply bioavailable Si.

Here, we applied two biochar materials differing in Si content on soils differing in weathering stage: a young Cambisol and a highly weathered Nitisol. We studied the impact of biochar supply on the bioavailability of Si, cotton biomass, and Si mineralomass. The biochar materials derived from, respectively: *Miscanthus* × *giganteus* (Mi; 34.6 g Si kg^{-1} in biochar) and soft woody material (SW; 0.9 g Si kg^{-1} in biochar). They were compared to conventional Si fertilizer wollastonite (Wo; $CaSiO_3$). Amendments were incorporated in soils at the rate of 3% (w/w). The content of bioavailable Si in soil was determined through 0.01 M $CaCl_2$ extraction.

In the Cambisol, the proportion ($CaCl_2$ extractable Si: total Si content) was significantly smaller for Mi (0.9%) than for Wo (5.2%). In the Nitisol, this proportion was much larger for Mi (1.4%) than for Wo (0.7%). Mi-biochar significantly increased Si-mineralomass relatively to SW-biochar in both soils. This increase was, however, much larger in the Nitisol (5.9-fold) than in the Cambisol (2.2-fold).

Mi biochar is thus an alternative Si fertilizer to Wo to supply bioavailable Si, increase plant biomass, and promote the biological cycle of Si in the soil-plant system in the Nitisol. Besides, it increased soil fertility and soil organic carbon content.

Key words: biochar / bioavailable silicon / cotton / soil desilication

1 Introduction

Silicon (Si) is ubiquitous in rocks and soils. Si is not essential but beneficial to plants. It increases photosynthetic activity and plant resistance against various biotic and abiotic stresses (*Belanger* et al., 1995; *Fauteux* et al., 2005; *Liang* et al., 2007). Aqueous monosilicic acid ($H_4SiO_4^0$) is ubiquitous in soil solution where plant roots take it up. In plants, mass flow transports $H_4SiO_4^0$ upwards to transpiration sites. Therein, water loss increases $H_4SiO_4^0$ concentration and induces polymerization through Si–O–Si bounds, and further precipitation of hydrated amorphous silica as phytoliths (amorphous $SiO_2 \cdot nH_2O$) (*Epstein*, 1994; *Ma* et al., 2006). Phytoliths (PhSi) are major biogenic silicate minerals (BSi). They return into the topsoil with dead plant materials and further contribute to the pool of dissolved Si (DSi) in soil (*Keller* et al., 2012) because of their solubility (*Fraysse* et al., 2009). They thus supply the pool of bioavailable Si in soils under forests (*Gérard* et al., 2008; *Cornelis* et al., 2011), grasslands (*Blecker* et al., 2006; *Alexandre* et al., 2011; *White* et al., 2012; *Issaharou-Matchi* et al., 2016) and croplands either in temperate conditions (*Vandevenne* et al., 2015) or in the humid tropics (*Henriet*

et al., 2008). The contribution of PhSi to DSi pool can be substantially impacted by land use (*Struyf* et al., 2010; *Barão* et al., 2014), harvest exportation (*Keller* et al., 2012; *Vandevenne* et al., 2012, 2015), soil weathering stage (*Henriet* et al., 2008) and, overall, soil processes (*Cornelis* and *Delvaux*, 2016).

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

Biochar is a black carbon (C) used as a soil amendment. It is produced by heating organic matter under oxygen-limited con-

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ditions. Pyrolysis converts organic substances into stable C compounds, hence preserves atmospheric C (*Lehmann* et al., 2011; *Lehmann* and *Joseph*, 2015). Applied to soil, biochar retains and supplies plant nutrients (*Glaser* et al., 2002; *Lehmann* et al., 2003; *Laird* et al., 2010), increases soil C stock (*Lehmann* and *Joseph*, 2015), soil pH and plant growth (*Biederman* and *Harpole*, 2013). Black C significantly increases soil cation exchange capacity (CEC) through its large surface charge density and surface area (*Liang* et al., 2006). Yet the effect of biochar on plant growth largely depends on soil properties and biochar types (*Jeffery* et al., 2011; *Biederman* and *Harpole*, 2013; *Crane-Droesch* et al., 2013).

Pyrolysis of plant residues concentrates PhSi minerals (*Houben* et al., 2014), which in turn contribute to supply DSi (*Houben* et al., 2014; *Xiao* et al., 2014), and increase Si uptake by plants (*Liu* et al., 2014). The impact of both the PhSi content of biochar and soil Si availability on plant growth and Si uptake is, however, unknown. Here, we used two biochars differing in Si content and applied them on soils differing in weathering stage, respectively, a young Cambisol and an old, highly weathered Nitisol. We studied the release of DSi after biochar application. We further investigated the effect of biochar on soil fertility, plant biomass, and Si mineralomass, and compared it to the one of $CaSiO_3$-wollastonite.

2 Materials and methods

2.1 Biochar, wollastonite and soils

2.1.1 Biochars and wollastonite

The biochars were produced by industrial pyrolysis (550°C, heating rate 65 °C min^{-1}, kiln residence time 12 min) at UK Biochar Research Centre (UKBRC), respectively from *Miscanthus* (*Miscanthus × giganteus*; Mi) and soft wood (Mixed softwood pellets; SW) (Tab. 1). The wollastonite (Wo) was provided by R.T Vanderbilt Company, Inc. (Norwalk, CT, USA) (Tab. 1). In the following text, the biochars and wollastonite are considered as soil amendments.

2.1.2 Soils and soil:amendment mixtures

The two soils key out as, respectively, a Dystric Cambisol (CA) and a Rhodic Nitisol (NI) in the WRB system (*IUSS*, 2014). CA (Forest of Lauzelle, Louvain-la Neuve, Belgium)

developed from quaternary calcareous silty loess under humid temperate conditions (*Titeux* and *Delvaux*, 2009). NI is a paleosol from the quarry of Transinne (Belgium), formed under humid tropical paleo-conditions. The quarry exhibits a deep 65-m saprolithic profile derived from Early Devonian bedrock, containing kaolinite, resistant muscovite and quartz, and Fe oxyhydroxides (*Thiry* et al., 2006). The soil samples were air-dried and sieved at 2-mm. The soil : amendment mixtures were made at 100 : 3 (g : g; dry soil weight), and are named CA-Mi, CA-SW, CA-Wo, NI-Mi, NI-SW, and NI-Wo.

2.2 $CaCl_2$ extraction of Si

The extraction was carried out on the Si amendments, soils and soil : amendment mixtures before the cotton pot experiment. The $CaCl_2$-extractable Si content ($CaCl_2$-Si) was determined using a 5g : 50 mL (0.01 M $CaCl_2$) soil : solution ratio, and a 5 h continuous shaking time (*Haysom* and *Chapman*, 1975). After centrifuged at 3,000 *g* for 20 min, the supernatant was separated for analysis. The residues were submitted to five successive extractions during 5 d. The concentration of Si was measured in each extract by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

2.2.1 Analyses

pH was measured in, respectively, H_2O and KCl 1M, with 5g : 25 mL suspensions. The CEC and content of exchangeable cations were determined using CH_3COONH_4 1 M buffered at pH = 7 (*Chapman*, 1965). Elemental analysis was carried out after calcination and Li-metaborate + Li-tetraborate fusion (*Chao* and *Sanzolone*, 1992). The elemental contents were determined by ICP-AES. Elemental contents of alkaline and alkaline-earth cations were summed up as the total reserve in bases (TRB), which estimates the content of weatherable minerals (*Herbillon*, 1986). Total carbon (C) and nitrogen (N) contents were measured by dry combustion with a CNS analyzer (Flash EA1112 Series).

2.2.2 Scanning Electron Microscopy (SEM)

The analyses of biochar particles were performed on specimens using a JEOL FEG SEM 7600F, equipped with Energy Dispersive X-ray Spectrometry system (EDX, Jeol JSM2300 with a resolution < 129 eV) operating at 15 keV with a working distance of 8 mm for the element detection. The acquisition time for the chemical spectra lasted 100 s with a probe current of 1 nA.

Table 1: Selected properties of the soft wood (SW), *Miscanthus* (Mi) biochars and wollastonite (Wo): pH$_{water}$, total contents of Carbon (C), Nitrogen (N), $CaCl_2$ extractable Si ($CaCl_2$-Si), major alkaline and alkaline-earth cations (Ca, Mg, K, Na), and silicon (Si).

Amend-ments	pH H$_2$O	C[b] (%)	N[b]	$CaCl_2$-Si (g kg^{-1})	Ca (g kg^{-1})	Mg	Na	K	Si
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[a]	8.87 (1.04)	314.71 (2.54)	10.80 (0.06)	< 0.01	1.10 (0.06)	233.34 (2.03)

[a]nd means not determined;
[b]Single measurements only.

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2.3 Plant material and analyses, pot experiment

2.3.1 Cotton plant

We used *Gossypium hirsutum*, var (STAM 59A-Bollgard II) from southern Burkina Faso.

2.3.2 Pot experiment in a phytotron (5 months)

The soil : amendment mixtures (100 : 3, g : g) were irrigated with deionized water and allowed to equilibrate for a week at 70% of field water holding capacity before planting. After germination in deionized water, the plantlets were allowed to grow up to 5 cm. They were then transplanted into pots (7.5 L) containing the respective soil : amendment mixtures (3kg dry weight), in triplicate under 28°C and relative humidity at 80%. Each pot was watered every three days with 33 mL deionized water during the first two months, and 100 mL the last three months. No nutrients were supplied. We collected the aboveground plant part after 5 months for further drying at 55°C during 7 d prior to biomass weighing.

2.3.3 Analyses

Mineral analysis was carried out after calcination at 450°C for 1 d and fusion in Li-metaborate + Li-tetraborate at 1,000°C (*Chao* and *Sanzolone*, 1992), followed by ash dissolution with concentrated HNO_3. Element contents were measured by ICP-AES. Element mineralomass was computed from total element contents and cotton biomass.

2.4 Statistical analyses

We used the SPSS 17.0 statistical software to carry out the one-way analysis of variance (ANOVA) (at $p < 0.05$ level) and LSD (at $p < 0.05$ level).

3 Results

3.1 Properties of the biochars and wollastonite

As shown in Tab. 1, the OC content (%) was 84.9 in SW, 77.1 in Mi, and 0.6 in Wo. The total N content (%) 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) 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 that of Mi (34.6 g kg^{-1}), and 259 times larger than in SW (0.9 g kg^{-1}). The contents of Ca and Mg in Wo were also significantly larger than in Mi and WS. The contents of K (cmol$_c$ kg^{-1}) were larger in Mi (14.9) than in SW (2.6) and Wo (1.1). Figure 1 illustrated the SEM micrographs and associated EDX spectra of biochar materials SW and Mi. In particular, Fig. 1f showed the occurrence of dumbbell-shaped, fine silt-sized phytoliths in Mi biochar. As inferred from Fig. 1e, they were abundant and undamaged after pyrolysis at 550°C.

3.2 Soil and soil:amendment properties

CA and NI are acid soils since their pH$_{water}$ values were 4.6 and 5.2, respectively (Tab. 2). C and N contents, CEC and contents of exchangeable cations were larger in CA than in NI. Of course, biochar application resulted in a huge increase

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.

| Treat-ments	pH		C	N	CEC	Exchangeable cations				BS
						Ca^{2+}	K$^+$	Na$^+$	Mg^{2+}	
	H$_2$O	KCl	(g kg^{-1})			(cmol$_c$ kg^{-1})				(%)
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
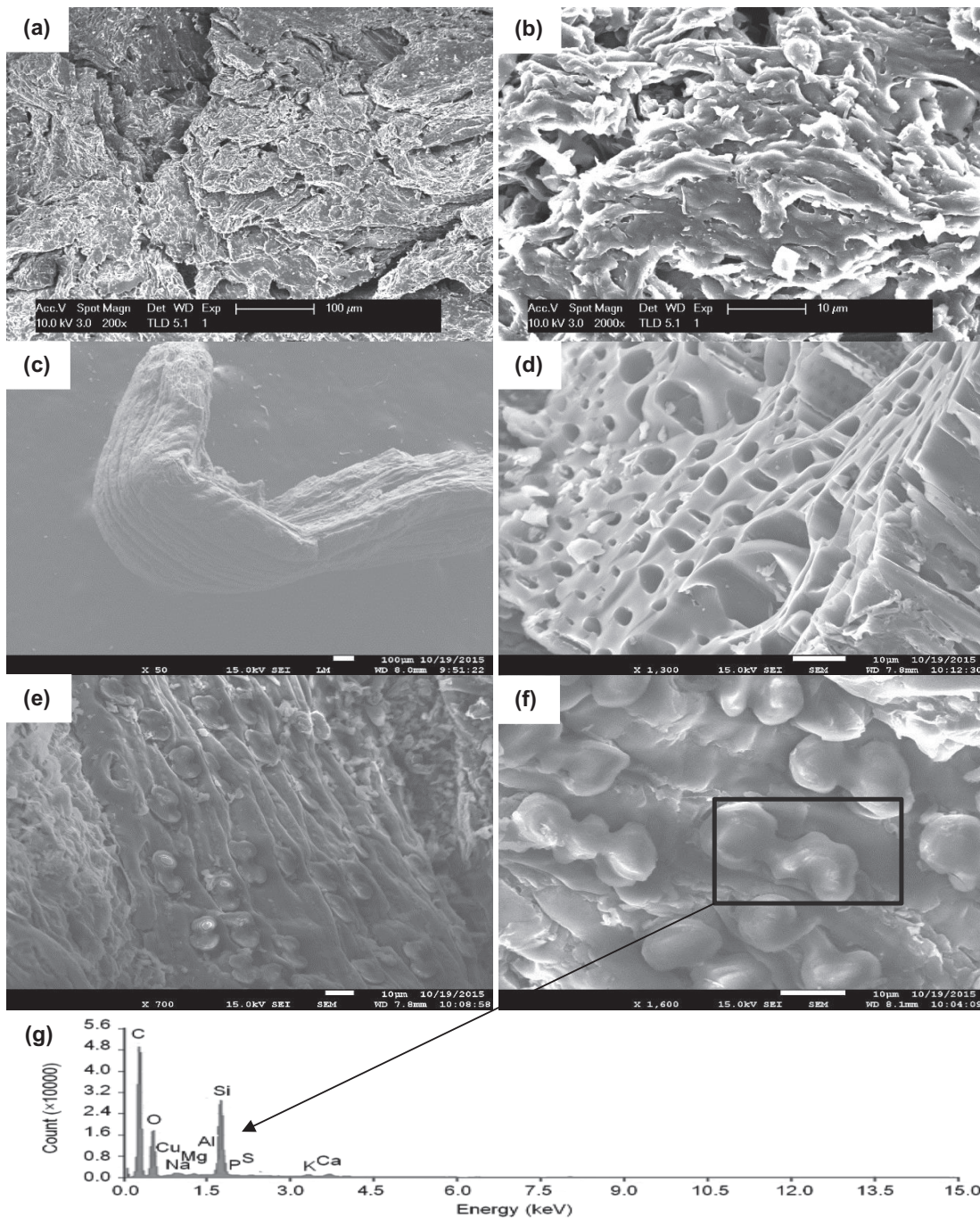
Figure 1: Scanning electron micrographs (SEM) images of biochar materials from soft wood (a, b) and *Miscanthus* (*Miscanthus* × *giganteus*) straws (c, d). (e) and (f) are the SEM images of *Miscanthus* phytoliths. The energy dispersive X-ray spectra (EDX) (g) collected from (f), shows the dominance of C, O, and Si, hence documenting the presence of phytoliths ($SiO_2 \cdot nH_2O$).

in C content while Wo did not. The latter application led to a marked increase in pH and content of exchangeable Ca. SW application did not generate any change of pH, CEC, contents of exchangeable cations and base saturation whatever the soil type. To the contrary, Mi application induced a significant increase of these parameters. In particular, exchangeable K content ($cmol_c$ kg^{-1}) increased from, respectively, 0.2 to 0.97 in CA, and 0.05 to 0.81 in NI. From total contents of Al and Fe (g kg^{-1}) amounted to, respectively, 39.2 and 18.5 in CA,

96.5 and 30.6 in NI (Tab. 3). Total Si content (g kg^{-1}) in CA and NI was 376.8 and 311.9, respectively. Computed values of Si/(Al+Fe) atomic ratio were thus larger in CA (7.5) than in NI (2.7). TRB ($cmol_c$ kg^{-1}) amounted to 112 in CA and 99 in NI. Residual weatherable minerals in CA were plagioclase, feldspar, and soil clay minerals. From Fig. 2, CA clay minerals consisted of kaolinite and an assemblage of 2:1:1 and 2:1 clay minerals involving chlorite, illite, vermiculite, and smectite. NI distinctly differed by the large dominance of well crys-
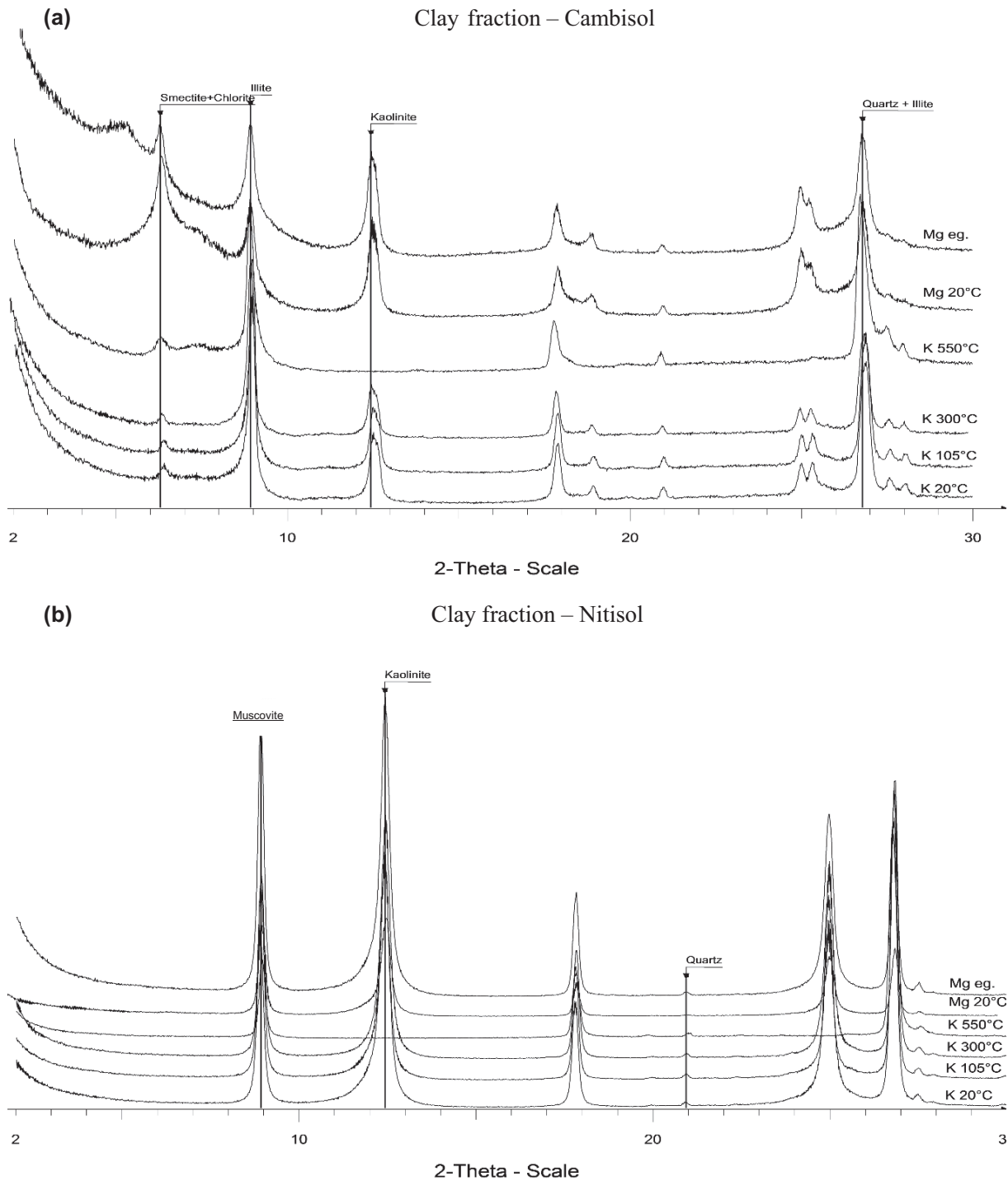
(a) Clay fraction – Cambisol

(b) Clay fraction – Nitisol

Figure 2: XRD patterns of the clay-size fraction (< 2 μm) 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.

tallized muscovite and kaolinite. In the Nitisol, K was by far the largest dominant cation in TRB, in line with the occurrence of muscovite, a dioctahedral mica resistant to weathering. The large amount of non-exchangeable K (Tab. 3) thus hided the advanced weathering stage of NI because muscovite is stable and does not weather in soils. The reserve of weatherable minerals was then estimated by the difference between TRB and the content of non-exchangeable K, excluding

K-bearing muscovite. [TRB-K] (cmol$_c$ kg^{-1}) amounted to 72.5 in CA and 22.1 in NI, indicating the strongly advanced weathering stage of NI. [TRB-K] did not increase following biochar application. To the contrary, wollastonite application 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. Cumulative CaCl$_2$-Si (mg kg^{-1}) (Tab. 3, Fig. 3) was significantly larger in CA (34) than in NI (24). CaCl$_2$-Si significantly (*p* < 0.01)
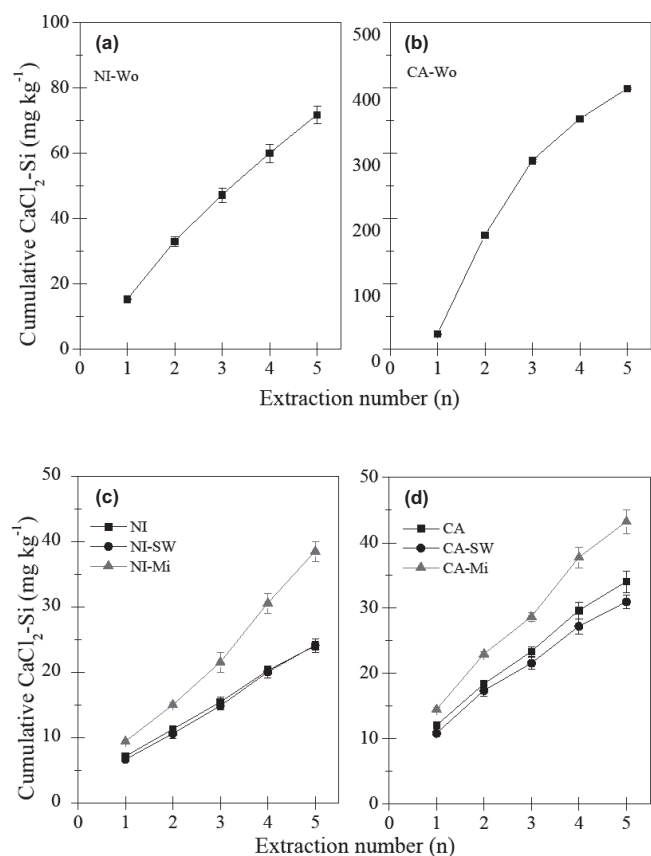
Figure 3: Plot of the cumulative amount of $CaCl_2$ extractable Si content against the extraction number (the Si content at each number is added to the Si contents extracted following the preceding(s) extraction(s) in (a, b) soil : wollastonite (a, b: NI-Wo and CA-Wo); (c) NI, NI-Mi and NI-SW, and (d) CA, CA-Mi and CA-SW.

increased after Wo application in CA (398.7) and NI (71.7). Unlike SW, Mi significantly ($p < 0.01$) increased $CaCl_2$-Si in CA (43.2) and NI (38.5).

3.3 Biomass and mineralomass of cotton plants

The cotton biomass (g plant^{-1}) was significantly larger in CA (8.6) than in NI (0.32) (Tab. 4). Mi significantly increased cotton biomass, by 84% in CA, and 368% in NI. Mi significantly increased plant mineralomass of Ca, K, and Mg in both soils. Plant Si mineralomass (mg plant^{-1}) was, by far, significantly larger in CA (10.6) than in NI (0.8). Relatively to SW, Mi significantly increased the plant Si content (g Si 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 CA-Mi and 1.12 for NI-Mi. Si mineralomass indeed increased by 120% in CA-Mi and 180% in NI-Mi relatively to the untreated soils CA and Mi.

4 Discussion

4.1 Weathering stage of soils

The values of TRB and Si/(Al+Fe) ratio as well as the nature of secondary clay minerals are used to assess soil weather-

ing stage (*Herbillon*, 1986). Taking into account the stability of muscovite in soils, NI exhibited an advanced weathering stage characteristic of strongly weathered ferrallitic soils (*Herbillon*, 1986). In CA, the large dominance of quartz is characteristic of soils of the Belgian loess belt, in which the reserve of weatherable minerals is concentrated in the clay fraction (*Brahy* et al., 2000). CA soil clay minerals (kaolinite, chlorite, illite, vermiculite and smectite; Fig. 2a) revealed a mineralogical assemblage typical of moderately weathered soils under temperate climates. To the contrary, NI soil clay minerals (Fig. 2b) make an assemblage typical for desilicated, highly weathered soils formed under humid tropical conditions. Consequently, $CaCl_2$-Si content was significantly larger in CA than in NI (Fig. 3).

4.2 Mobility of Si in soil : amendment mixtures

As it is linked to the DSi pool from which plant roots take up Si, $CaCl_2$-Si could quantify the pool of bioavailable Si in soils (*Sauer* et al., 2006). Cumulative $CaCl_2$-Si (mg kg^{-1}) was significantly larger in 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 (30.9), and NI-SW (24.1) (Tab. 3; Fig. 3). Wo is indeed an efficient Si fertilizer releasing bioavailable Si. For each amendment, $CaCl_2$-Si was systematically smaller in NI : amendment mixtures. Part of $H_4SiO_4^0$ released by amendments was undoubtedly adsorbed by oxide surfaces in NI as it commonly occurs in highly weathered soils (*Herbillon* et al., 1977).

To further assess Si mobility, we define the efficiency of each amendment (AM) using $CaCl_2$-Si and total Si contents (Tab. 3) as follows:

$$\frac{(CaCl_2 - Si \text{ in soil} : AM) - (CaCl_2 - Si \text{ in soil})}{Total \text{ } Si \text{ content of } AM} \times 100. \qquad (1)$$

In CA, the efficiency of Mi was significantly smaller (0.9%) than that of Wo (5.2%). To the contrary, in NI, Mi efficiency was larger (1.4%) than to the one of Wo (0.7%). Possibly phytolith solubility could be larger in NI-Mi because of a larger pH. Besides, the release of bioavailable Si was significantly larger for Mi than for SW (Fig. 3c, d). The ample reserve of PhSi in Mi *vs.* SW (34.6 *vs.* 0.9 g Si kg^{-1}; Tab. 1) and the accessibility of phytoliths in Mi (Fig. 1e, f) support that phytoliths readily contribute to DSi. They resist to pyrolytic temperatures as high as 550°C and further dissolve to release DSi given their solubility (*Fraysse* et al., 2009). Since their dissolution rate increases with increasing pH in the range of pH 3–12 (*Fraysse* et al., 2006), the ability of phytolith-rich Mi to supply DSi is enhanced by pH increase, especially in NI, where silica sorption increased pH of surrounding solution. Indeed, Fe oxides adsorb Si in soils (*Jones* and *Handreck*, 1963, 1967) and control DSi (*McKeague* and *Cline*, 1963).

The release of bioavailable Si in Mi-amended soils was not affected by soil type and weathering stage. The biochar derived from high-Si accumulator *Miscanthus* is thus an alternative Si fertilizer to wollastonite to supply bioavailable Si in the highly weathered Nitisol.

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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[a]	Total Si	Total elements				TRB[b]	[TRB-K][c]	Total elements		Si/(Al+Fe)
			Ca	K	Na	Mg			Al	Fe	
	(mg kg^{-1})	(g kg^{-1})	(cmol$_c$ kg^{-1})						(g kg^{-1})		
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

[a]Cumulative amount after 5 extractions (see also Fig. 3);
[b]TRB is the sum of total contents of Ca, Mg, Na and K in soil (*Herbillon*, 1986);
[c]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

4.3 Effect of biochar amendment on soil properties

As already reported (*Sohi* et al., 2010; *Van Zwieten* et al., 2010), biochar application to soils affects their properties (Tab. 2). The impact depends, however, on the types of biochar and soil. Supplying ash biochar induces a change of pH and nutrient availability (*Clarholm*, 1994; *Mahmood* et al.,

2003). Here, applying biochar did not significantly modify CEC in CA. However, it slightly increased CEC in NI, but only after Mi application, which also increased the contents of exchangeable cations, namely K and Mg in CA-Mi, and Ca, K, Na, and Mg in NI-Mi (Tab. 2). Such increases were not observed after SW addition. Since applying Mi increased the effective CEC (ECEC), we hypothesize that it is due to an increase of surface area and surface charge density of biochar particle as previously reported for black C (*Liang* et al., 2006). The pH rise, in turn, undoubtedly led to increase ECEC (*Glaser* et al., 2002; *Laird* et al., 2010; *Houben* et al., 2014). Relatively to SW, Mi contained more ashes and initial exchangeable and non-exchangeable cations (Tab. 1, Fig. 1). Mi thus had a larger ability to increase pH and ECEC as observed by *Houben* et al. (2014). Furthermore, the improvement of soil properties was more pronounced in NI-Mi than in CA-Mi. Base saturation (BS %) significantly increased in both CA-Mi and NI-Mi, reflecting the ability of Mi biochar to enhance nutrient availability (Tab. 3) as predicted by *Liang* et al. (2006) for black C. The larger BS after Mi amendment was due to the larger nutrient content (Ca, Mg, and K) in Mi relatively to SW (Tab. 1). The impact of Mi biochar on soil fertility was thus positive, particularly in the highly weathered Nitisol, though at a very low level tested in non-fertilized soil.

4.4 Effect of biochar amendment on cotton biomass and Si mineralomass

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

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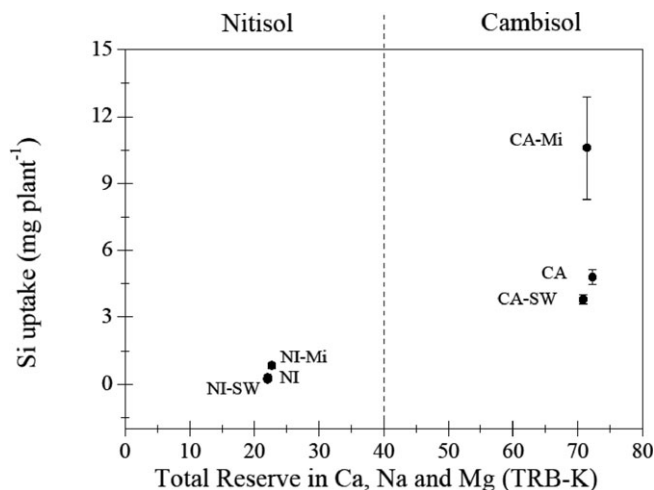

Figure 4: Plot of Si uptake by cotton plants against the total reserve of Ca, Mg, and Na minerals (excluding K-bearing muscovite) in the Cambisol (CA) and Nitisol (NI).

Si uptake by cotton plants markedly differed between CA and NI (Fig. 4). After Mi application, Si uptake increased 5.9-fold in NI and 2.2-fold in CA, keeping in mind that biomass (g plant⁻¹) was very low in NI (0.2–1.5) compared to CA (8.8–16.2) (Tab. 4). As discussed above, phytoliths were abundant in Mi; they dissolved and released DSi, thereby contributing to the pool of bioavailable Si, which was readily taken up by plant roots (Figs. 1–3; Tab. 3). This effect was particularly important in the highly weathered Nitisol depleted in primary and secondary silicates.

5 Conclusion

Miscanthus biochar and wollastonite amendments significantly ($p < 0.01$) enhanced the release of $CaCl_2$-extractable Si in a young Cambisol and an old, highly weathered Nitisol. Soft wood biochar amendment had no effect on the release of $CaCl_2$-extractable Si in both soils. *Miscanthus* biochar supply increased ECEC, particularly the content of exchangeable K, while soft wood biochar did not have any effect on these parameters whatever the soil type. Both biochar amendments induced a significant effect on C and N contents in both soils. *Miscanthus* biochar generated a significant increase of cotton biomass. That increase was, however, larger in the Nitisol than in the Cambisol, since it was 4.7-fold in the former and 1.8-fold in the latter. In terms of Si uptake after Mi application, the increase in the Nitisol (5.9-fold) was much larger than in the Cambisol (2.2-fold), supporting a larger efficiency of Si release from *Miscanthus* phytoliths in the Nitisol.

Our data thus highlight that *Miscanthus* biochar is an alternative Si amendment to wollastonite to supply bio-available Si, increase plant biomass, and promote the biological cycle of Si in the soil–plant system. This positive impact of a Si-rich biochar is, however, larger in the old, desilicated, highly weathered Nitisol. Overall, it demonstrates that Si is progressively released from phytolith-rich biochar and directly contributes to the pool of bioavailable Si for plant root uptake in

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soil. This is particularly important for agro-ecosystems in which high-Si accumulator plants grow in highly weathered, desilicated soils. Further field experiments are required to confirm the effect of phytolith-rich biochar as a Si fertilizer over the whole plant cycle. Furthermore, the efficiency of various biochar types to release Si and plant nutrients should be studied.

Acknowledgments

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