

Phytolith-rich biochar: A potential Si fertilizer in desilicated soils

Zimin Li  | Bruno Delvaux

Earth and Life Institute, Soil
Science, Université catholique de Louvain
(UCLouvain), Louvain-la-Neuve, Belgium

Correspondence

Zimin Li, Earth and Life Institute, Soil
Sciences, Université catholique de Louvain
(UCLouvain), Croix du Sud 2/L7.05.10,
1348 Louvain-la-Neuve, Belgium.
Email: zimin.li@uclouvain.be

Funding information

Fonds De La Recherche Scientifique -
FNRS, Grant/Award Number: FC49049;
Université Catholique de Louvain

Abstract

Silicon (Si) is beneficial to plants since it increases photosynthetic efficiency, and alleviates biotic and abiotic stresses. In the most highly weathered and desilicated soils, plant phytoliths make up the reservoir of bioavailable Si. The regular removal of crop residues, however, substantially decreases this pool. Si supply may therefore be required to sustain continuous cropping. Available Si fertilizers are costly and usually poor in soluble Si. Biochar produced from the pyrolysis of phytolith-rich biomass is thus a promising alternative Si source for plants. Taking into account the challenges of increasing food demand and environmental concerns, we evaluate the global potential of biochar produced from major crop residues and manures in terms of phytogenic Si (PhSi) supply. Crop residues contribute to 80% of the global production of biomass dry matter (8,201 Tg/year) of which 3,137 Tg/year are potentially available after pyrolysis, giving a potential application rate of $1.7 \text{ T ha}^{-1} \text{ year}^{-1}$ for highly weathered soils in the tropics. The potential PhSi supply from crop biochar amounts to 102 Tg Si/year. On its own, rice straws produce 57.7 Tg PhSi/year, accounting for 56.6% of the potential annual PhSi production. The Si release from crop biochar depends on inter alia feedstock type, pyrolysis temperature, soil pH, and buffer capacity. Furthermore, the amplitude of plant Si uptake and mineralomass depends on plant species, soil properties, and processes. These factors interact and can exert a decisive influence on the effectiveness of phytolith-rich biochar in releasing Si into highly weathered soils. We conclude that the use of phytolith-rich biochar as a Si fertilizer offers undeniable potential to mitigate desilication and to enhance Si ecological services due to soil weathering and biomass removal. This potential must be explored, as well as the conditions for using biochar in the field.

KEYWORDS

biochar, highly weathering soil, phytolith, silicon, sustainable agriculture

1 | INTRODUCTION

Biochars are organic materials produced by the pyrolysis of a highly diverse range of feedstocks including plant biomass, manures, or organic waste products (Demirbas, 2004; Gaunt & Lehmann, 2008; Lehmann, Gaunt, & Rondon,

2006). The pyrolytic process is a slow combustion carried out at low oxygen supply, traditionally between 300 and 700°C (Boateng, Garcia-Perez, Mašek, & Brown, 2015). As illustrated in Figure 1, pyrolysis increases the degree of aromatic carbon, highly disordered in an amorphous mass (Chia, Downie, & Munroe, 2015). Besides, the oxidation

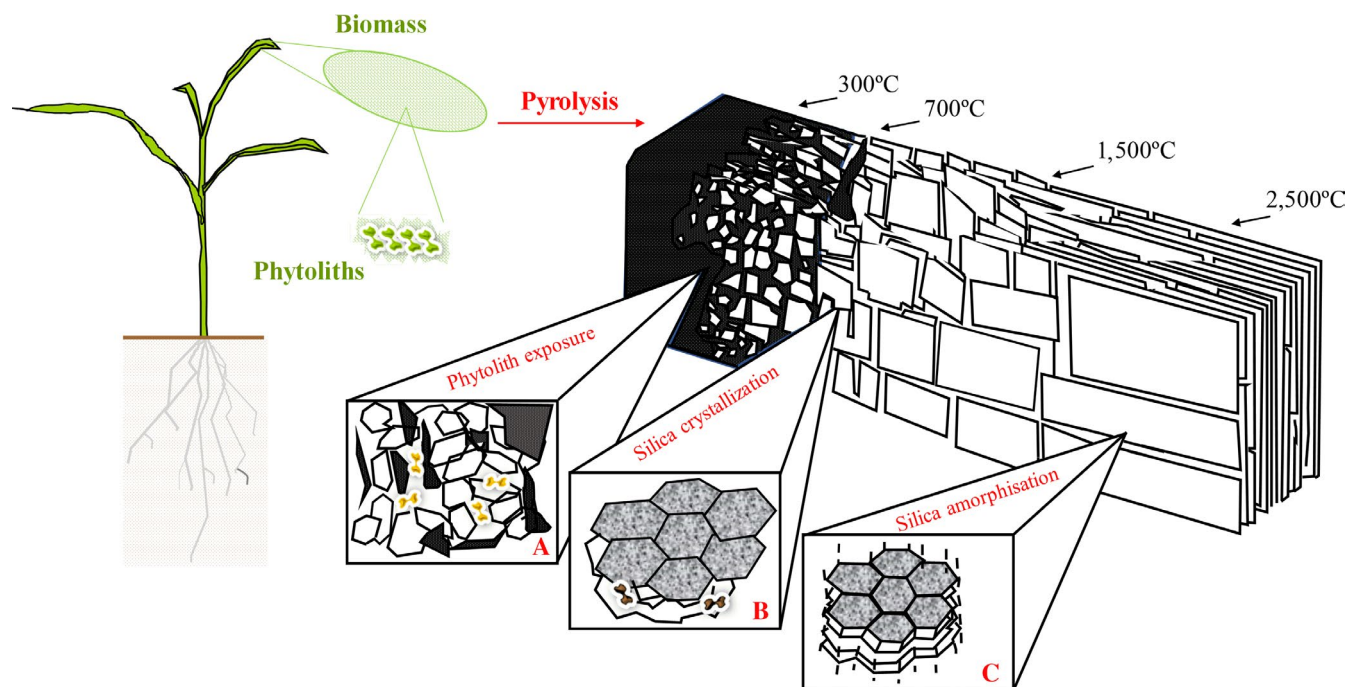


FIGURE 1 Schematic illustration of the organic carbon (OC)–phytogenic Si structural interaction relative to pyrolysis process. (A) The pyrolytic process (300–700°C) increases the degree of aromatic OC, highly disordered in amorphous mass, and exposes phytolith particles to the surrounding environment. (B) Further heating above 500–700°C generates growing sheets of turbostratic aromatic carbon, and promotes silica crystallization: phytoliths transform into cristobalite and/or tridymite and eventually quartz. (C) The structure becomes graphitic with order in the third dimension whereas crystalline silicates are amorphized at high temperatures. The heating process from (A) to (C) is accompanied by a decrease in the apparent volume and an increasing organization. Adapted from Chia et al. (2015)

process increases the capacity of the pyrolyzed matter to retain nutrients, and the resilience of carbon in soil (Liang et al., 2006). Regarding the recent interest in the use of biochars in agricultural soils, Sanchez (2019) notes that burnt organic carbon (OC) is a major component of soil humus in areas where periodic burning is common, such as in many tropical savannas and in slash-and-burn systems. This author further reports that the most iconic effect of biochars in soils occurs in the fertile black earths, so-called *Terra preta* (Sombroek, Nachtergaele, & Hebel, 1993) widely found in ancient Amazonian settlements, where large quantities of charcoal, organic residues, ashes, etc., were added over long periods of time by previous civilizations (Glaser & Woods, 2004; Lehmann et al., 2003). The production of pyrolyzed organic substances by humans is thus very old, but the scientific interest and agronomic potential were only recently developed. It is clear that the issue of climate change is part of this high interest because of the potential offered by biochars to store carbon in soil (Lehmann & Joseph, 2015). From recent literature data, both biochar production and supply to agrosystems are recommended as a promising multiple-“win” strategy for a number of benefits, inter alia (i.a.) the disposal of crop residue (Jeffery et al., 2015; Van Zwieten et al., 2010; Woolf, Amonette, Street-Perrott, Lehmann, & Joseph, 2010) and the sequestration of

OC to mitigate climate change (Lehmann, 2007; Lehmann et al., 2006; Schlesinger & Amundson, 2019; Weng et al., 2017). Besides, biochar application does not only lead to increase soil pH and nutrient retention (Chan & Xu, 2009; Laird et al., 2010; Sohi, Krull, Lopez-Capel, & Bol, 2010; Van Zwieten et al., 2010) but also decreases the toxicity of contaminants in soil (Houben, Evrard, & Sonnet, 2013; Lu et al., 2017; Nie et al., 2018; O'Connor et al., 2018; Yang, Lu, et al., 2017), thus promoting crop biomass and yield (Biederman & Harpole, 2013; Crane-Droesch et al., 2013; Jeffery et al., 2011; Liu et al., 2013).

However, the potential of biochars as a source of silicon (Si) to alleviate advanced soil desilication in vast tropical croplands is poorly known despite the beneficial effects of Si in terms of plant protection against biotic and abiotic stress (Belanger, 1995; Cooke & Leishman, 2016; Coskun et al., 2019; Fauteux, Rémus-Borel, Menzies, & Bélanger, 2005; Liang, Sun, Zhu, & Christie, 2007; Ma, 2004). In fact, a large part of crop production is lost due to harmful pests and diseases, while the remainder is threatened by increasingly erratic weather and soil fertility decline (Sanchez, 2019; Vanlauwe & Giller, 2006). In challenging these global change issues, the accumulation of Si in cereals provides protection against pests and pathogens, and mitigates the impacts of climatic stresses such as drought and salinity (Coskun et al., 2019; Meunier

et al., 2017). Si-based plant protection could therefore open new avenues to enhance crop yields by addressing current threats and contribute to improving food security, enhancing bioenergy production, and mitigating climate change. Several cultivated plants are high Si-accumulators. In particular, monocotyledons, notably cereals and sugarcane, actively take up dissolved silica (Deshmukh & Bélanger, 2016) which precipitates in plant tissues as amorphous silica bodies named phytolith (McKeague & Cline, 1963), a phytogenic silica (PhSi; Cooke & Leishman, 2016; McKeague & Cline, 1963; Puppe et al., 2017; Sommer et al., 2013). Once deposited into soil within organic debris, phytoliths can dissolve and provide plant-available Si (McKeague & Cline, 1963). Pyrolyzed phytolith-rich biomass can thus be regarded as a source of bioavailable Si (Wang, Xiao, & Chen, 2018; Xiao, Chen, & Zhu, 2014), which can be taken up by plant roots and increase crop biomass (Li, Song, Singh, & Wang, 2019; Li, Unzué-Belmonte, et al., 2019). Besides, the biochar supply improves soil fertility and C sequestration (Houben, Sonnet, & Cornelis, 2014; Wang, Wang, & Wang, 2018). Generalizations about biochars performance must, however, be balanced against the fact that biochars are highly heterogeneous in their form and reactivity in soil, which may affect the dynamics of dissolved Si (DSi) in soil. In addition, as illustrated in Figure 1, the pyrolytic process may impact the intrinsic properties of phytoliths (Jindo, Mizumoto, Sawada, Sanchez-Monedero, & Sonoki, 2014; Wang, Wang, et al., 2018; Wu, Yang, et al., 2012; Wu, Wang, & Hill, 2012; Xiao et al., 2014).

Here, we review the available literature to evaluate the prospect of using phytolith-rich biochar to reduce our reliance on expensive Si fertilizer inputs. In particular, we first provide global estimates of PhSi biochar and then evaluate their potential to challenge agronomic and environmental issues. This knowledge is essential to develop guidelines for the selection and appropriate use of biochars to achieve desired agronomic outcomes. We particularly focus on the potential use of PhSi-rich biochar in highly weathered soils. Except for Podzols, the distribution of which is confined to cold and forested areas, the most weathered soils occur in the tropics where desilicated Ferralsols, Acrisols, Lixisols, and Nitisols make up roughly 2,385 Mha (Driessen, Deckers, Spaargaren, & Nachtergaele, 2000; IUSS, 2014), of which approximately 1,890 Mha are cultivated in input-free cropping systems (Sanchez, 2019).

2 | ENHANCING THE BIOLOGICAL SI FEEDBACK LOOP IN AGROECOSYSTEMS

Over the past decades, several studies have highlighted the importance of the soil–plant cycle of Si, notably on the transfer of this element from terrestrial to marine ecosystems, linking

the global cycles of Si and carbon (Carey & Fulweiler, 2012; Cermeño, Falkowski, Romero, Schaller, & Vallina, 2015; Conley & Carey, 2015; Lahr, Bosak, Lara, & Mitchell, 2015; Li, Lerman, & Mackenzie, 2011; Liang, Nikolic, Bélanger, Gong, & Song, 2015; Parr & Sullivan, 2005; Reyerson et al., 2016; Sommer, Kaczorek, Kuzyakov, & Breuer, 2006; Song, Wang, Strong, Li, & Jiang, 2012; Street-Perrott & Barker, 2008; Struyf & Conley, 2012; Tréguer & Pondaven, 2000; Trembath-Reichert, Wilson, McGlynn, & Fischer, 2015). As illustrated in Figure 2, the primary source of readily or plant-available Si is the reserve of lithogenic silicate minerals (LSi). LSi dissolution releases aqueous H_4SiO_4^0 (DSi), which may follow four routes: formation of pedogenic silicate minerals (PSi), adsorption onto Al and Fe oxide surfaces, uptake by plant roots, and to watersheds through drainage waters. Besides, Si can be taken up by diverse organisms in soils (Desplanques et al., 2006; Puppe, Ehrmann, Kaczorek, Wanner, & Sommer, 2015). In fact, silica structures synthesized by, for example protists, sponges, and plants, form protistic, zoogenic, and PhSi pools in soils, respectively (Puppe et al., 2015). These pools represent various sources of DSi in agricultural soils (Haynes, 2017), because biogenic silica has a much higher dissolution rate than silicate minerals (Frayse, Pokrovsky, Schott, & Meunier, 2006, 2009). The phytogenic pool is, however, the most important source of bioavailable Si in soil.

Once taken up by plant roots, H_4SiO_4^0 is transferred to plant shoot tissues where it precipitates as silica bodies ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) named phytoliths (PhSi; Jones & Milne, 1963), which return to soil within plant debris (Smithson, 1956). Soil phytoliths readily dissolve at common pH values of soil solution (Frayse et al., 2006, 2009), and thus contribute to feed the reservoir of plant-available Si (Alexandre, Meunier, Colin, & Koud, 1997; Bartoli, 1983; Farmer, Delbos, & Miller, 2005; Keller, Guntzer, Barboni, Labreuche, & Meunier, 2012; Li, Song, & Cornelis, 2014; Marxen et al., 2016; Meunier, Guntzer, Kirman, & Keller, 2008; Riotte et al., 2018; Unzué-Belmonte et al., 2016; Yang & Zhang, 2018). As defined in Figure 2, the mineral Si contribution and biological Si feedback loops interact in the Si soil–plant cycle. According to Cornelis and Delvaux (2016), in natural ecosystems, the relative importance of the mineral Si contribution is greatest at the early stage of soil weathering, but sharply decreases at the advanced weathering stage where phytoliths start to alleviate natural soil desilication and mainly feed the pool of plant-available Si (Lucas, Luizao, Chauvel, Rouiller, & Nahon, 1993; Meunier, Colin, & Alarcon, 1999).

The past decade has also seen the emergence of studies that confirm the crucial role of Si in agriculture (Carey & Fulweiler, 2016; Guo et al., 2015; Haynes, 2014; Liang et al., 2015; Song, Müller, & Wang, 2014) and reveal the impact of land use on the pool of plant-available Si (Barão

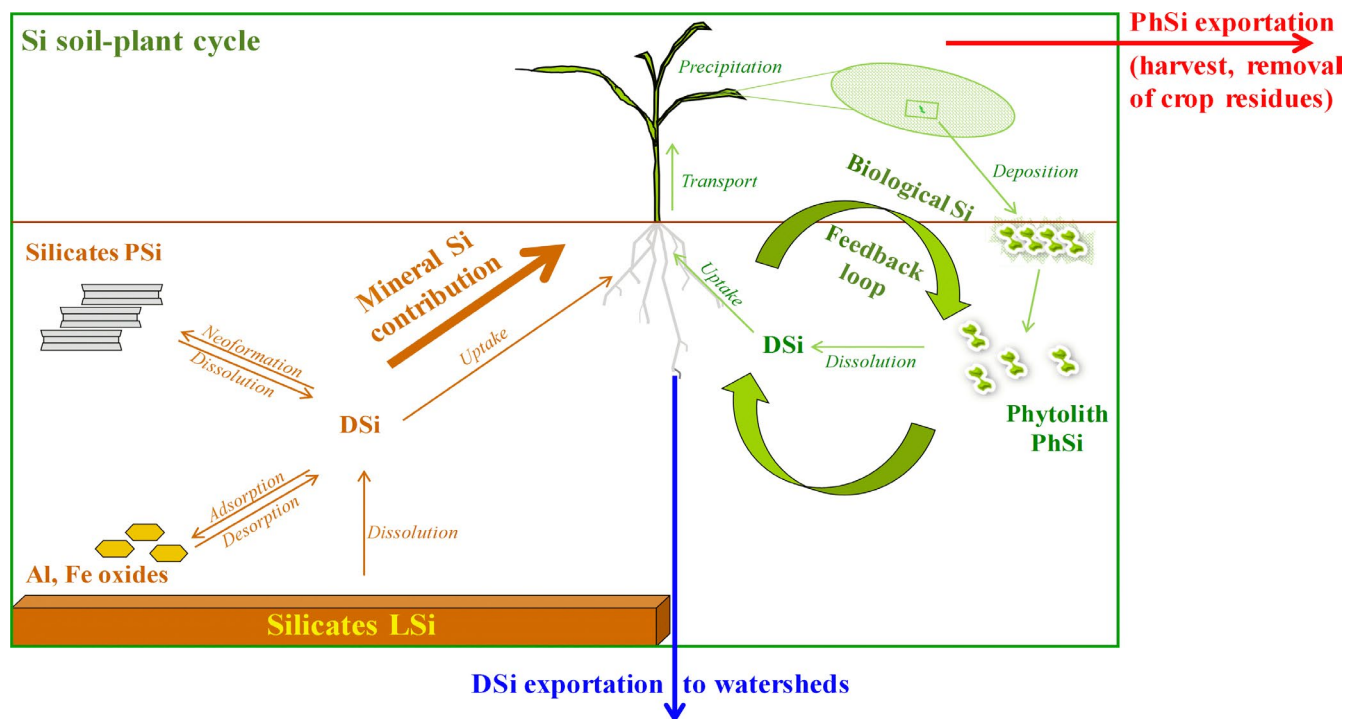


FIGURE 2 Conceptual scheme of Si reservoirs and fluxes in the soil–plant system. The original source of dissolved Si (DSi; H_4SiO_4^0) is the pool of primary weatherable lithogenic silicates (LSi). DSi may take four routes in this system: (a) formation of pedogenic silicate minerals (PSi); (b) adsorption onto Al, Fe oxide surfaces; (c) uptake by plant roots; (d) exportation to watersheds. In plant shoot tissues, H_4SiO_4^0 precipitates as phytolith, a phytogenic Si (PhSi). Processes (a) and (b) and their reverse reactions define the mineral Si contribution to DSi pool in the Si soil–plant cycle. DSi plant uptake, phytolith formation, return to soil, and dissolution define the biological Si feedback loop. PhSi can be exported out of the soil–plant system through crop harvesting and removal of crop residues. It is evident that, in highly weathered soils exhausted in LSi and depleted in PSi, the continuous loss of PhSi results in the increase in soil desilication. Adapted from Cornelis and Delvaux (2016)

et al., 2014; Clymans, Struyf, Govers, Vandevenne, & Conley, 2011; Conley et al., 2008; Guntzer, Keller, Poulton, Mcgrath, & Meunier, 2012; Struyf et al., 2010; Vandevenne et al., 2015; Vandevenne, Struyf, Clymans, & Meire, 2012). As illustrated in Figure 2, both the crop harvesting and removal of crop residues can disrupt the soil–plant cycle of Si and aggravate soil desilication, in particular in highly weathered soils (Henriet, Bodarwé, Dorel, Draye, & Delvaux, 2008; Klotzbücher et al., 2015). This threat must be challenged, given the role of Si in enhancing the photosynthetic activity and plant tolerance to various biotic and abiotic stresses (Belanger, 1995; Cooke & Leishman, 2016; Coskun et al., 2019; Fauteux et al., 2005; Hartley & Degabriel, 2016; Liang et al., 2007; Ma, 2004). Si fertilization indeed increases crop yields (Berthelsen, Noble, & Garside, 2001; Keller et al., 2012; Liang, Ma, Li, & Feng, 1994; Liang et al., 2015; Meyer & Keeping, 2001; Savant, Snyder, & Datnoff, 1996; Song, Wang, Strong, & Shan, 2014). It is increasingly practiced to improve crop productivity (Datnoff & Heckman, 2014; Datnoff, Snyder, & Korndörfer, 2001; Haynes, 2017; Keeping, 2017; Ma & Takahashi, 2002; Tubana, Babu, & Datnoff, 2016). To date, Si fertilizers consist mainly of silicate slag and natural silicate minerals (Berthelsen et al., 2001; Datnoff & Heckman,

2014; Gascho, 2001; Haynes, 2014; Haynes & Zhou, 2018; Keeping, 2017; Li et al., 2018; Liang et al., 1994; Ma & Takahashi, 2002), as well as nano-Si foliar fertilizers (Puppe & Sommer, 2018). Although cost-effective because they derive from by-products of furnaces, silicate slags often contain only a small proportion of soluble Si (Haynes, 2014, 2017; Liang et al., 2015; Savant et al., 1996), and may present hazardous levels of heavy metals (Belanger, 1995; Haynes, Belyaeva, & Kingston, 2013; Savant et al., 1996). In contrast, silicate minerals such as wollastonite (CaSiO_3) are expensive and have limited mineral reserves (Haynes, 2014; Haynes et al., 2013; Savant et al., 1996). More importantly, they do not improve soil fertility or store soil OC. More sustainable alternatives are thus needed to increase crop production and promote environment preservation. Using biochar is a promising alternative.

3 | PHSi BUDGETS IN CROPLANDS

3.1 | PhSi content in cultivated plants

The mechanisms of Si uptake by plants are active, passive, or rejective. Si accumulation in plants is caused by active

uptake, which is commonly attributed to the density of Si transporters in roots (Lsi1 and Lsi2) and shoots (Lsi6; Deshmukh & Bélanger, 2016; Exley, 2015; Ma et al., 2006, 2007; Ma & Yamaji, 2008; Mitani & Ma, 2005). Thus, Si content in plants is dependent on plant species, and varies from 0.1% to 10.0% of dry matter (DM; Epstein, 1999; Hodson, White, Mead, & Broadley, 2005). Based on Si contents, plant species can be classified as Si high-, low-, and non-accumulator, respectively (Takahashi, Ma, & Miyake, 1990). In this respect, Si high-accumulators generally contain 1.0%–10.0% Si in the DM, and are monocotyledons. Most dicotyledons take up Si passively, and their Si contents range from 0.5% to 1.0%. Some dicots, however, are unable to accumulate Si over 0.5% (Cooke, Degabriel, & Hartley, 2016; Hodson et al., 2005; Liang et al., 2007; Ma, Miyake, & Takahashi, 2001; Ma & Takahashi, 2002). However, biosilicification in plants may also follow passive uptake of Si (Exley, 2015). Crop residues from Si-accumulating plants may contain large amounts of Si so that their removal from croplands may significantly affect the terrestrial Si cycle (Carey & Fulweiler, 2012, 2016; Conley, 2002; Keller et al., 2012; Song, Parr, & Guo, 2013; Struyf et al., 2010; Vandevenne et al., 2012). Here, we focus on the PhSi content in rice hulls and straws, wheat straws, maize stalks and cobs, barley straws, sorghum straws, millet, rye and oats, sugarcane crop residues, oil crops including sunflower and cotton, legume crop residues including soybean straw and beans. As shown in Table S1, the highest PhSi contents are in rice hulls (10.3 wt%), rice straw (8.4 wt%), sugarcane (8.2 wt%), and millet (7.5 wt%), followed by straws of sorghum, wheat, maize, barley, and rye (1.9–6.0 wt%). In other crop residues, PhSi content is below 1.0 wt%. The differences in PhSi content among soybean straw and beans, sunflower, and cotton could be explained by various transpiration rates given the role of aquaporins in Si flux (Cooke et al., 2016; Deshmukh & Bélanger, 2016; Epstein, 2001; Hodson et al., 2005; Liang et al., 2007). In contrast, for cereals, Si is actively taken up, and the difference in PhSi content has been attributed to the density of Si transporters in plant roots (coded by the low-silicon genes Lsi1 and Lsi2) and in shoots (Lsi6; Liang, Si, & Römhild, 2005; Ma & Yamaji, 2008; Ma et al., 2007; Mitani & Ma, 2005). For example, compared to other crops, rice cultivars are well known to exhibit a stronger ability to accumulate PhSi due to a particularly high density of Si transporters in their roots (Epstein, 1999; Ma et al., 2006, 2007).

3.2 | PhSi amounts in crop residues and manures

Here, we do not consider crop residues belonging to the following three categories. First, the residues that are available in very small quantities (e.g., nut and peanut shells,

sesame, peas and orchard prunings) are neglected since they account for only 1.5% of global crop residues, their annual total dry biomass being below 6 Tg/year. Second, some residues exhibit relatively high water contents (e.g., potato) to be unsuitable for pyrolysis. Third, other residues, such as legume crops, exhibit no global significance because they have a very low PhSi content that is below 0.1% (Carey & Fulweiler, 2012, 2016; Hodson et al., 2005; Song et al., 2013). In Figure 3a, we estimate that the global PhSi annual production, as deduced from selected crops (Table S1), amounts to 213.8 Tg Si/year (Lal, 2005; Woolf et al., 2010). Our estimated annual PhSi amount is close to the global estimate (204.8 Tg BSi/year) of annual global crop straw provided by Carey and Fulweiler (2016). The total PhSi amount in crop residues depends on DM biomass, and on plant species or plant part (Table S1). In this regard, we distinguish the crop residues into five categories: rice, wheat, maize, sugarcane, and other crops with relatively low DM and PhSi content. Rice, wheat, maize, and sugarcane account for 194.1 Tg Si/year, that is, 90.8% of the total PhSi amount on a global scale (Figure 3a). Among these crop residues, rice straws and husks account for 83.4 Tg Si/year, and wheat straw accounts for 53.2 Tg Si/year. They thus contribute to 39.0% and 24.9% of the total global PhSi amount from crops, respectively. Thus, maintaining adequate PhSi stocks in agricultural systems is highly dependent on the recycling of rice and wheat crop residues. Since phytoliths are resistant to fungal or animal digestive juices after grass or crop feed ingestion, significant amounts of PhSi accumulate in animal manures (Hartley & DeGabriel, 2016; Jones & Handreck, 1967; Krishnan, Samson, Ravichandran, Narasimhan, & Dayanandan, 2000). We estimate that the global PhSi amount in selected manures (cattle, pig, and poultry) amounts to 42.0 Tg Si/year among which 94.5% is provided by cattle manures (Figure 3a). Manure return may thus play a major role in returning PhSi to soil, hence replenishing the pool of DSi in agricultural lands. Besides, the transit of phytoliths through animals can increase phytolith solubility: for example, applications of pig manure from rice straw-fed pigs at the rate of 35 Mg ha⁻¹ year⁻¹ significantly increased the content of plant-available Si in rice-cultivated soils (Song, Wang, et al., 2014).

3.3 | Removal of crop residues and subsequent exportation from croplands

The regular removal of crop straws of Si-accumulator plants is a common practice in agrosystems. The resulting Si exportation can lead to a substantial loss of PhSi in cultivated soils (Carey & Fulweiler, 2016; Guntzer, Keller, Poulton, et al., 2012; Keller et al., 2012; Vandevenne et al., 2012), creating a new loop in the soil–plant Si cycle. The loss of PhSi

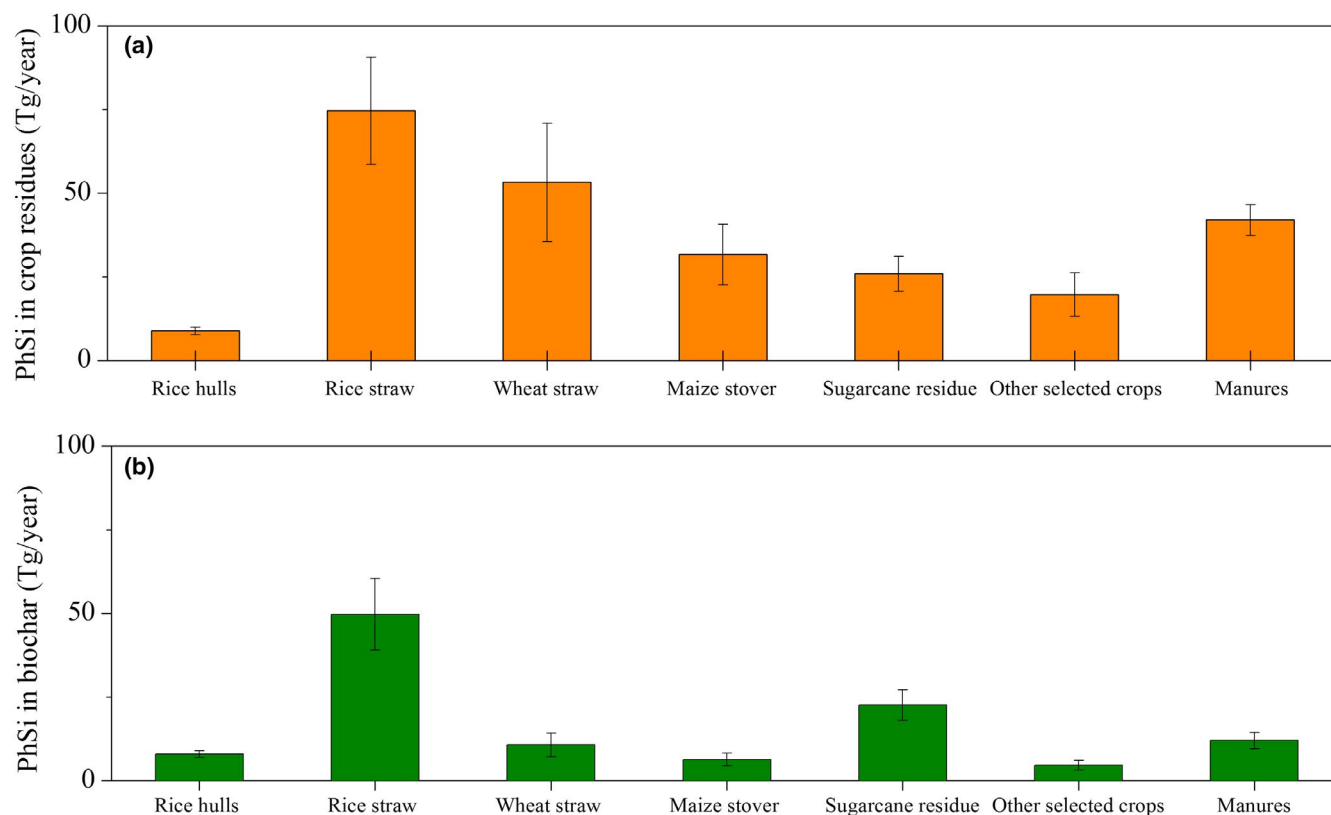


FIGURE 3 (a) Estimated annual global amounts of PhSi (Tg Si/year) in various crop residues and (b) their respective biochar products. These amounts were estimated using the data from Tables 1 and 2

is likely most pronounced under intensive agriculture, especially for Si high-accumulator crops (Table S1), since they pump large amounts of Si from soils. Carey and Fulweiler (2016) have indeed noted that, on a global scale, agricultural crops contribute to ~35% of PhSi accumulated by terrestrial plants because of their large biomass and PhSi contents (Table S1). They have also pointed out that this contribution will increase during the next decades because of increased agricultural production, predicting that the global removal of PhSi would reach 40 Tmol Si/year by 2050 (Carey & Fulweiler, 2016). Crop harvest and residue removal may thus substantially reduce soil PhSi (Meunier et al., 2008). This statement is supported by several studies. Clymans et al. (2011) report a threefold lower content of amorphous Si (ASi) in cultivated soils than in forest soils (22.8 vs. 66.9 t Si/ha) in southern Sweden, this difference resulting from the annual removal of PhSi from plant products and residues. Vandevenne et al. (2015) have reported that waters drained from arable cropland display heavier Si-isotopic composition ($\delta^{30}\text{Si}$) than the one from mature forest areas, resulting from the preferential removal of ^{28}Si in harvested plant parts. Annual exports of wheat straws led to a 10% decrease in the soil PhSi stock over 100 years (Guntzer, Keller, Poulton, et al., 2012), whereas the continuous removal of wheat straws at the rate of 50–100 kg Si ha⁻¹ year⁻¹ over the past 12 years would completely exhaust this pool within

next 10–20 years (Keller et al., 2012). Exporting PhSi out of rice croplands at 270 ± 80 kg Si ha⁻¹ year⁻¹ would consume the soil PhSi pool in next 5 years (Desplanques et al., 2006). These experimental data suggest that the depletion of the PhSi pool is caused by intensive cropping involving cereal straw removal. In contrast, returning rice straws to paddy soils maintained a constant stock of soil phytoliths and enriched it relatively to neighboring soils under bamboo and coniferous forest (Yang & Zhang, 2018). As recently reviewed (Vander Linden & Delvaux, 2019), the impact of soil weathering stage on the soil–plant Si cycle markedly differs depending on land use in the tropics. In less weathered soils, cultivated plants take up Si in larger amounts than forest trees do whereas in highly weathered soils, Si plant uptake increases in forest ecosystems while it decreases in croplands.

4 | PHYTOLITHS IN BIOCHARS PRODUCED FROM THE PYROLYSIS OF CROP RESIDUES AND MANURES

4.1 | Global amounts of PhSi in biochars derived from crop residues and manures

Using the conversion factor determined by Woolf et al. (2010), we estimate from Tables S1 and S2 the global

TABLE 1 Estimated global amounts of yearly produced PhSi (DM) in various crop residues and in their biochar products

Crop residues	Annual PhSi amount in crop residue (Tg Si/year)		Annual PhSi amount in biochar (Tg Si/year)	
	Mean	SD	Mean	SE
Cereals				
Rice hulls	8.8	1.2	7.9	1.0
Rice straw	74.6	16.0	49.8	10.7
Wheat straw	53.2	17.7	10.7	3.6
Maize stover	31.6	9.1	6.3	1.8
Barley straw	7.1	1.8	1.4	0.4
Sorghum straw	5.2	2.3	1.0	0.4
Rye straw	1.0	0.0	0.2	0.0
Millet straw	3.3	1.3	0.7	0.3
Oat straw	0.9	0.0	0.2	0.0
Total	185.7		78.1	
Sugar crop				
Sugarcane residue	25.8	5.2	22.6	4.5
Legume				
Soybean straw	1.3	0.4	0.9	0.3
Beans	0.4	0.3	0.3	0.0
Total	1.6		1.2	0.0
Oil crop				
Sunflower	0.4	0.0	0.3	
Cotton	0.2	0.0	0.2	0.0
Total	0.6		0.5	
Grand total	213.8		101.9	

Data are calculated from Table S1.

amounts of PhSi at 101.9 and 11.9 Tg Si/year in crop and manure biochars, respectively (Figure 3b; Table 1). They contribute to 82.3% and 17.7% of the global amounts of PhSi in crop and manure biochars, respectively. The amounts of PhSi vary depending on plant species and plant part, in particular on DM and initial PhSi content (Figure 3b). Rice straw is the largest driver of the global PhSi flow into biochar products since it contributes to 48.9% of the PhSi contained in crop biochars (Figure 3b), whereas sugarcane residues contribute to 22.7%. The contributions of wheat straws (10.5%), rice hulls (7.8%), and maize straws (6.3%) to the global PhSi reservoir in crop biochars are relatively low (below 11%). Maintaining an adequate global PhSi reservoir through biochar supply in agricultural soils thus requires to produce biochar from rice straws and husks, sugarcane residues, wheat and maize straws. Though the global DM production (Tg/year) is much larger for cattle manure (1,570) than for pig (90) and poultry (134) manures (Table S2), the conversion factor into biochar is 1/3.9 for cattle, 1/1.1 for pig and poultry

TABLE 2 Estimated global amounts of yearly produced PhSi in manure (DM) and in their derived biochars

Manures	Annual PhSi amount in manure (Tg Si/year)		Annual PhSi amount in biochar (Tg Si/year)	
	Mean	SD	Mean	SD
Cattle manure	39.7	0.0	9.9	0.0
Pig manure	1.6	0.3	1.4	0.3
Poultry manure	0.7	0.0	0.6	0.0
Total	42.0	0.3	11.9	0.3

Data are calculated from Table S2.

manures, revealing a much lower potential of cattle manure for biochar production and agricultural use as compared to pig and poultry manures (Hoogwijk et al., 2003; Woolf et al., 2010). However, cattle manure is enriched in PhSi (Table 2), which originates from fodder obtained from Si-accumulating plants (Blecker, McCulley, Chadwick, & Kelly, 2006; Hartley & DeGabriel, 2016). In contrast, pig and poultry manures are comparatively poor in PhSi (Table 2). Cattle manure is thus the largest driver of the global PhSi flow into manure biochar since it contributes to 83.2% of the PhSi produced by manure biochars (Figure 3b). The PhSi pool in cattle manure biochar may thus affect the soil PhSi pool in grasslands. Unfortunately, this is poorly studied.

4.2 | Effect of pyrolysis on phytolith content and morphology

Biochar yield is the percentage of pyrolyzed DM in relation to the original dry biomass. It depends on pyrolysis temperature, heating rate, and feedstocks (Ronsse, Hecke, Dickinson, & Prins, 2013; Spokas & Reicosky, 2009; Van Zwieten et al., 2010). Biochars produced after slow pyrolysis below 700°C exhibit yields as high as ~50% (Yang, Wang, et al., 2017), and optimal effects on plant-available nutrients (Atkinson, Fitzgerald, & Hipps, 2010; Chan & Xu, 2009; Sohi et al., 2010), whereas they concentrate Si (Xiao et al., 2014), which is preserved as phytolithic Si. PhSi content in rice straw biochar (RS) raises from 49.0 to 142.1 mg/g from 150 to 700°C. Phytoliths resist to pyrolytic heating (Kelly, 1990; Parr, 2006), and keep their initial morphological characteristics below 500–700°C (Elbaum, Weiner, Albert, & Elbaum, 2003; Piperno & Pearsall, 1998), depending on plant species. The morphology of phytoliths from pyrolyzed tree leaves (*Morus alba*, *Pteroceltis tatarinowii*, *Celtis bungeana*, *Celtis koraiensis*, etc.) is not altered up to 500°C, but can be slightly altered above that temperature (Wu, Wang, et al., 2012). In contrast, phytoliths from pyrolyzed grasses are more resistant

since their morphology only slightly alters above 700°C (Parr, 2006; Wu, Wang, et al., 2012; Yin, Yang, & Zheng, 2014). Phytoliths are firmly entrenched to the surface of *Miscanthus* biochar particles pyrolyzed at 600°C (Houben et al., 2014). Phytoliths of rice husk lose their distinct morphological characteristics above 900°C, and completely disappear at 1,100°C (Wu, Wang, et al., 2012; Yin et al., 2014). These experimental facts suggest that the recommended pyrolysis temperature would be below 500°C for tree or wood material, and at 600°C for grass materials but not above 700°C for rice husk.

4.3 | Phytolith transformation

Increasing pyrolytic temperature increases the content of ASi in biochar. For rice straw, ASi content increases from 49.8 to 148.6 mg/g from 150 to 500°C, but decreases from 500 to 700°C (Figure 4b). This change results from the transformation of phytoliths upon heating (Shinohara & Kohyama, 2004; Wu, Wang, et al., 2012; Xiao et al., 2014), which follows the sequence: hydrated amorphous silica→amorphous silica→cristobalite or tridymite→quartz

(Bettermann & Liebau, 1975). Phytoliths precipitate as hydrated ASi ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) in living tissues through inorganic polymerization (Jones & Milne, 1963; Piperno & Pearsall, 1998). Their morphology changes with increasing temperature (Bettermann & Liebau, 1975; Elbaum et al., 2003; Jones & Milne, 1963). Amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ is relatively stable below 150°C (Elbaum et al., 2003; Kelly, 1990; Parr, Dolic, Lancaster, & Boyd, 2001). Heating from 150 to 500°C weakens the H bonds of the hydrated ASi, allowing polymeric, crystal nucleation and growth. Silica crystallization results from an intense cracking of C components, enhancing the exposition of phytolith particles to dehydration, polymerization, and crystallization (Nguyen, Dultz, & Guggenberger, 2014; Xiao et al., 2014). Above 500°C, phytoliths are completely exposed, and undergo diagenesis toward crystalline forms, that is, from cristobalite and tridymite into quartz (Nguyen et al., 2014; Shinohara & Kohyama, 2004; Xiao et al., 2014). X-ray diffraction easily detects cristobalite and tridymite in rice straws pyrolyzed at 700°C. Above 700°C, phytolith transformation causes a change in the refractive indices of the silicate mineral (Elbaum et al., 2003; Jones & Milne, 1963).

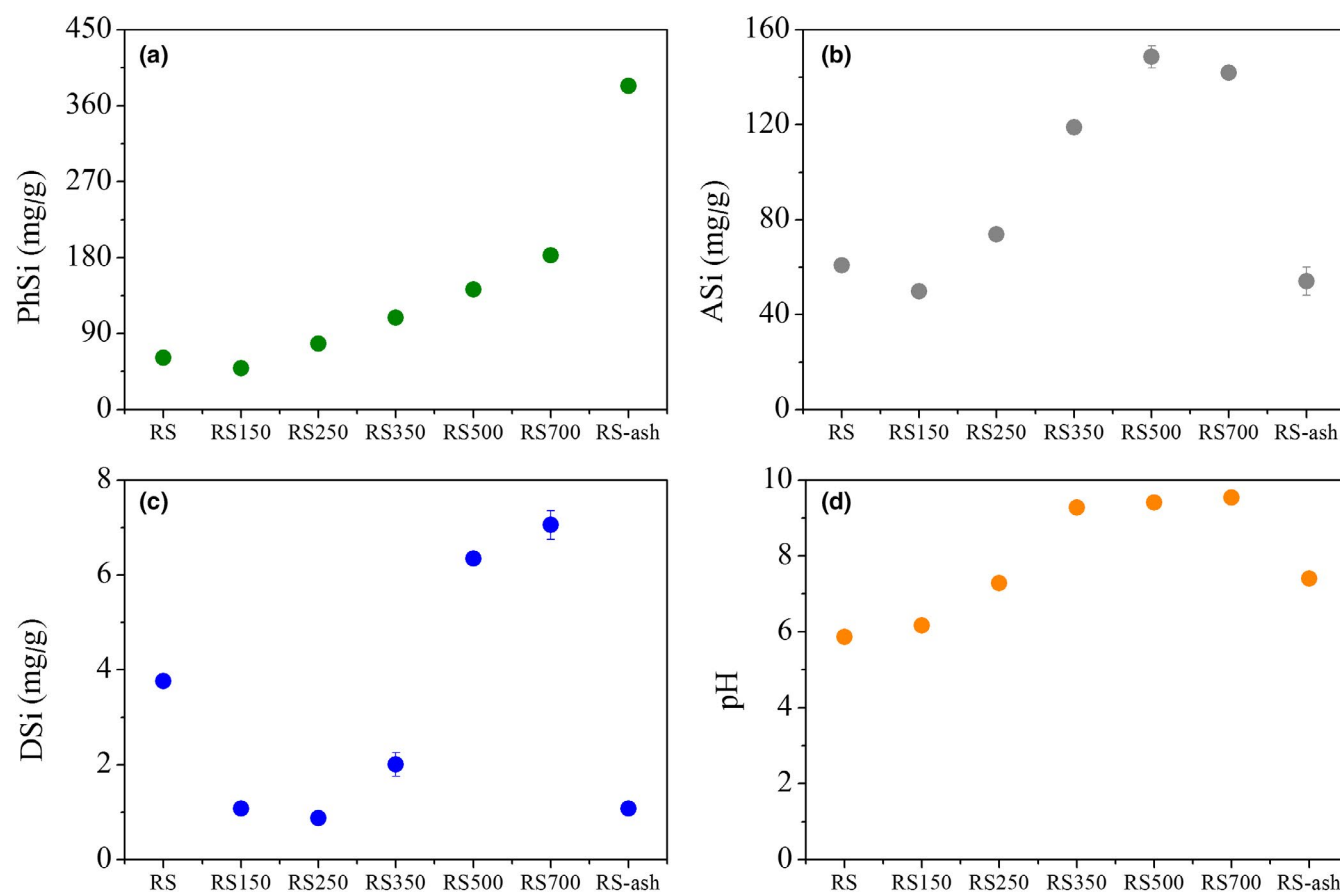


FIGURE 4 Contents of (a) phytogenic Si (PhSi), (b) amorphous Si (ASi), (c) dissolved Si (DSi), and (d) pH values in rice straw (RS) and its biochars pyrolyzed at different temperatures (150, 250, 350, 500, and 700°C), as well as in the ash residue (RS-ash). Note: Data are from Xiao et al. (2014). ASi (0.5 M NaOH extracts). DSi and pH as measured in 0.02 M CaCl_2 extracts

4.4 | DSi release from biochar phytoliths

Pyrolysis enhances phytolith dissolution, relative to original unheated PhSi particles and silica in ash. Biochar phytoliths readily dissolve and release DSi (Houben et al., 2014; Li et al., 2018). Their dissolution rate depends on their intrinsic properties as impacted by pyrolysis such as their amorphous character, surface area, surface acidity or alkalinity, fixed C, and pH of surrounding solution. Let us discuss these factors here below. First, as discussed above, pyrolysis has a major effect on PhSi concentration in biochar (Figure 4a), and thus on ASi content and potential Si release, particularly at 500–700°C (Figure 4b,c). In this range of temperatures, however, phytolith dissolution can be limited above 500°C (Cabanes, Weiner, & Shahack-Gross, 2011; Nguyen et al., 2014; Wang, Xiao, et al., 2018). Experimental results show that the release of DSi is maximal for biochars derived from rice husks at 700°C (Wang, Xiao, et al., 2018), and at 400–500°C for biochars derived from rice and wheat straws (Cabanes et al., 2011; Nguyen et al., 2014). Above 500°C, tridymite and/or cristobalite form, but they are much less soluble than phytoliths (Dove & Elston, 1992; Fraysse et al., 2006; Iler, 1979). Second, the dissolution of unheated phytolith is largely pH dependent (Fraysse et al., 2009). The pH dependence of DSi release from biochar

has been reported by Liu et al. (2014). With increasing pH, phytolith dissolution is enhanced by increasing deprotonation of silanol groups $\equiv\text{Si}-\text{O}^-$ (Brady & Walther, 1990), which favors the breaking of siloxane bonds $>\text{Si}-\text{O}-\text{Si}<$, and enhances the nucleophilic properties of water (Dove, 1995) or polarizing surface Si–O–Si bonds (Brady & Walther, 1990). The dissolution rate of unheated phytoliths increases by two orders of magnitude from pH 4 to 8 (Fraysse et al., 2009), whereas the one of heated phytoliths from rice straw biochar increases fourfold from pH 4.5 to 6.5 (Nguyen et al., 2014). In this respect, another advantage of biochars is their liming effect since pyrolysis markedly increases the pH of the pyrolyzed material (Ippolito, Spokas, Novak, Lentz, & Cantrell, 2015; Xiao et al., 2014). Figure 4d illustrates the increase of pH from 6.1 to 9.6 with increasing temperature and the concomitant increase in DSi release (Figure 4c). The liming effect can be strengthened by a KOH pretreatment of biochars, which enhances the release of DSi (Wang, Wang, et al., 2018). Third, since they govern the balance of cations and anions released into the liquid phase (Atkinson et al., 2010; Silber, Levkovitch, & Graber, 2010), the surface acidity or alkalinity of biochars can affect the release of mineral nutrients (K, Ca, Fe, Na, and Mg), and that of Si (Figures 4c and 5a,b). As illustrated in Figure 5, the pyrolysis of rice straws increases the surface area, fixed C, and

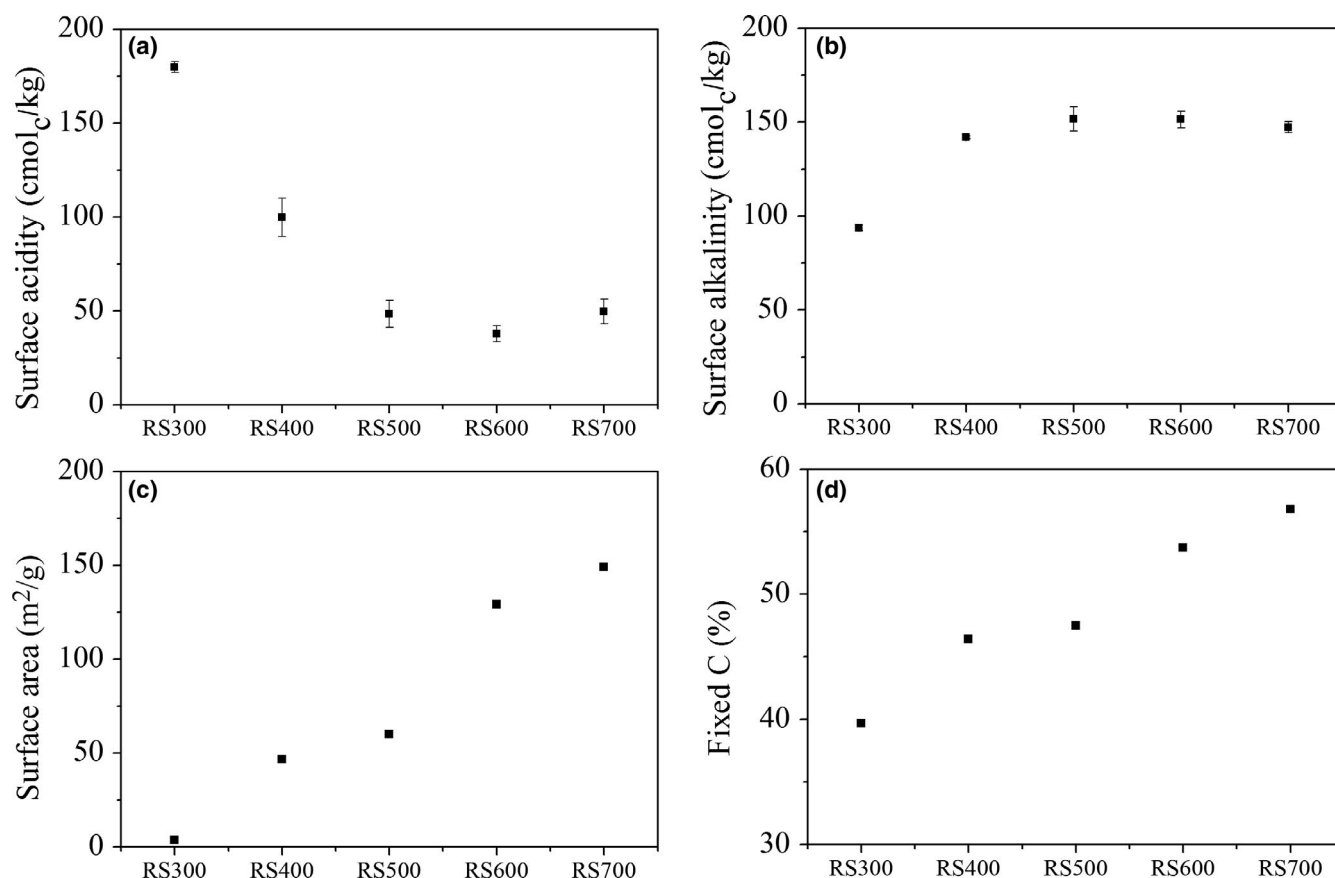


FIGURE 5 (a) Surface acidity, (b) surface alkalinity, (c) external, BET-N₂ surface area, and (d) fixed C in the rice straw RS-derived biochars at different pyrolytic temperatures (300, 400, 500, 600, and 700°C). Adapted from Wu, Yang, et al. (2012), Jindo et al. (2014), and Wang, Xiao, et al. (2018)

surface alkalinity of derived biochar, but decreases its surface acidity. Anions such as COO^- and PO_4^{3-} may interact with tetrahedral Si of deprotonated phytolith silanol groups by replacing OH^- groups, hence controlling phytolith dissolution. Yet inorganic anions are more effective in increasing phytolith solubility than organic anions (Nguyen et al., 2014). In contrast, the adsorption of monovalent cations (Na^+ , K^+) onto deprotonated phytolith Si-O^- groups could impede the hydration of Si-O-Si bonds in the siloxane surface and depress Si release (Nguyen et al., 2014). The adsorption of Al species on phytolith surface may decrease the release of DSi (Bartoli & Wilding, 1980; Nguyen et al., 2014), whereas the adsorption of Fe and Al species significantly decrease the release of DSi from biochars (Qian, Chen, & Chen, 2016; Wang, Xiao, et al., 2018). Fourth, phytolith dissolution also depends on particle size and thus on surface area, a high surface area enhancing phytolith dissolution (Bartoli, 1985; Bartoli & Wilding, 1980; Cabanes et al., 2011; Fraysse et al., 2009; Piperno, 2006; Puppe & Leue, 2018; Sommer et al., 2013; Wilding & Drees, 1974; Wilding, Hallmark, & Smeck, 1979). Small-sized biochar particles release larger amounts of plant available nutrients and Si than large-sized biochars do (Chan & Xu, 2009; Silber et al., 2010; Sohi et al., 2010; Van Zwieten et al., 2010). The enlarged surface area (Figure 5c) favors the access of hydroxyl ions to Si-O-Si bonds, and accelerates phytolith dissolution (Figure 4c). High surface area biochars are known to adsorb efficiently heavy metals (Beesley & Marmiroli, 2011; Houben et al., 2013; Reddy & Lee, 2014; Yang et al., 2016; Zhang et al., 2013), Al (Qian & Chen, 2013; Qian et al., 2016), and other inorganic ions (Beesley & Marmiroli, 2011; Chan & Xu, 2009; Dai et al., 2016; Raveendran, Ganesh, & Khilar, 1995; Wang, Xiao, et al., 2018), because of their large internal porosity (Chia et al., 2015). Last, but not least, it is worth noting that a mutual protection occurs between C and PhSi in biochar (Guo & Chen, 2014; Xiao et al., 2014), suggesting the potential of biochar for C sequestration. This protection is, however, dependent on pyrolytic temperature as it is enhanced at low pyrolytic temperatures (Xiao et al., 2014; Figures 4 and 5). At high pyrolytic temperatures, phytolith exposure increases (Figure 1), hence DSi release increases (Figure 4c).

5 | AGRONOMIC POTENTIAL OF PHYTOLITHIC BIOCHAR

Despite its non-essentiality for plants, Si offers a great agronomic potential because it increases the photosynthetic efficiency, and alleviates various biotic and abiotic stresses (Belanger, 1995; Fauteux et al., 2005; Liang et al., 2007). The need of supplying Si is particularly acute in highly weathered soils, which are depleted in weatherable LSi and PSi silicates. In these soils, phytoliths make the pool of plant-available Si (Alexandre et al., 1997; Li, Unzué-Belmonte, et

al., 2019; Lucas et al., 1993; Meunier et al., 1999). Since phytoliths can be exported through the removal of crop residues, PhSi depletion may aggravate soil desilication in these soils, making them candidates for external Si supply. However, in the tropics, most farmers are unable to use Si fertilizers at recommended rates of 1 or 2 t ha⁻¹ year⁻¹ since silicate slag and minerals are expensive and limited worldwide (Savant et al., 1996). Supplying phytolithic biochar produced from crop residues is a potential and environmentally friendly Si fertilizer, which has additional well-known effects on soil fertility through the increase in CEC, pH, and bioavailable nutrients.

5.1 | Plant-available Si

The amount of DSi effectively available for plants depends on biochar type, soil properties, and processes since DSi may be involved in PSi formation, adsorbed on secondary oxides or leached out and transferred to watersheds, as well as taken up by various organisms. Houben et al. (2014) have shown that bioavailable Si content significantly differed between distinct biochars (*Miscanthus x giganteus* straws, coffee husks, and woody material), *Miscanthus* being particularly rich in PhSi. Wang, Wang, et al. (2018) have reported significant differences in DSi release from biochars in the following order: rice straw > *Miscanthus* straw > sugarcane harvest residue > switchgrass, due to their differences in initial amounts of PhSi. Regardless of pyrolysis temperature, Wang, Xiao, et al. (2018) reported that rice husk biochar had a larger PhSi content than rice straw, wood sawdust, and orange peel, and that bioavailable Si in soil was much larger when released from rice husk biochar. Figure 6 shows that the application of wheat straw biochar increases the content of bioavailable Si, and the Si content of rice shoots (Liu et al., 2014).

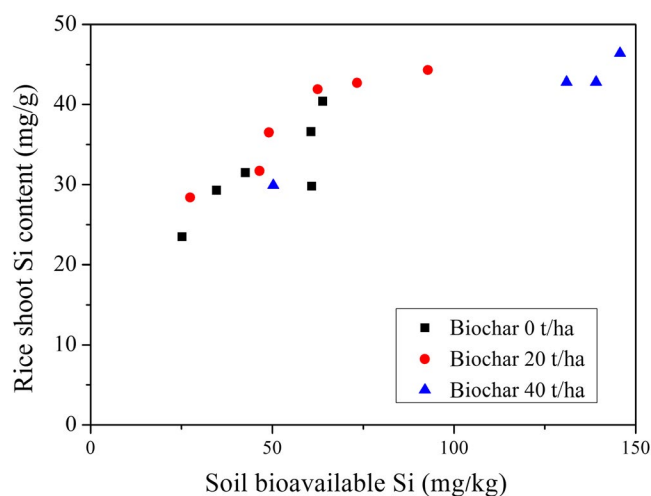


FIGURE 6 Rice plant shoot Si content (mg/g) after wheat-straw biochar application as plotted against soil bioavailable Si as extracted by 0.025 M citric acid (field data from Liu et al., 2014)

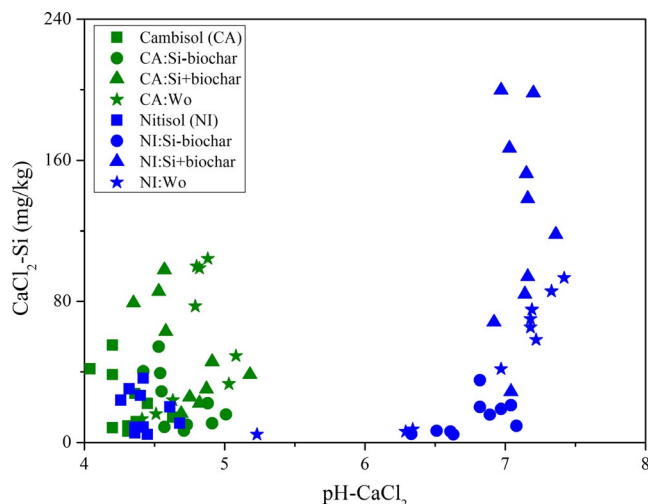


FIGURE 7 Plot of $\text{CaCl}_2\text{-Si}$ content against pH-CaCl_2 in soil, soil:biochar, and soil:wollastonite—solution systems. *Note:* Wo: wollastonite (CaSiO_3) is a common Si fertilizer; Si – biochar is free of PhSi, whereas Si + biochar is enriched in PhSi. The Cambisol and the Nitisol have a high and a very low buffer capacity, respectively. Wo and Si + biochar supplies are identical in terms of Si addition. Adapted from Li, Unzué-Belmonte, et al. (2019)

Soil properties and processes affect the release of DSi from biochar phytoliths. Through its regulation of soil pH, soil buffering capacity controls the dissolution of biochar phytoliths in soils (Figure 7; Li, Unzué-Belmonte, et al., 2019). Figure 7 further shows that at a given supply of phytolith biochar, the liming effect of biochar depends on soil buffering capacity and this effect is crucial to predict the mobility of Si in the soil–plant system (Li, Unzué-Belmonte, et al., 2019). Adsorption process may retrieve DSi from soil solution and decrease Si plant availability. H_4SiO_4^0 adsorption onto Al, Fe oxides is enhanced in highly weathered soils (Meunier, Sandhya, Prakash, Borschneck, & Dussouillez, 2018) where natural soil desilication results in the relative accumulation of Al, Fe oxides, which selectively adsorb H_4SiO_4^0 . Thus, at given PhSi biochar supply, soil properties and processes chiefly govern the plant availability of Si. The efficiency of PhSi biochar supply is thus expected to vary largely according to soil type.

5.2 | Alleviation of toxicities

Crop biochars are low-cost sorbents for soil contaminants that are either organic or metallic (Ahmad et al., 2014; Ali et al., 2017; Beesley et al., 2011; Houben et al., 2013; Inyang et al., 2016; O'Connor et al., 2018; Yang, Lu, et al., 2017; Zhang et al., 2013). Alleviating the toxicity of organic substances is observed in biochar, but after pyrolysis performed at low temperatures (Ahmad et al., 2014). Because of their high surface area, internal porosity, surface precipitation, and sorption capacity, crop biochars significantly alleviate heavy

metal toxicity in contaminated soils (Abbas et al., 2017; Verheijen, Jeffery, Bastos, & Velde, 2010). The liming effect of biochars promotes the deprotonation of organic ligands and thus their binding with heavy metals, especially Pb and Cu (Houben et al., 2013; Uchimiya, Chang, & Klasson, 2011; Yang et al., 2016; Yang, Lu, et al., 2017; Zhang et al., 2013). In addition, the coprecipitation of DSi with heavy metals may occur (Belanger, 1995; Cooke & Leishman, 2016; Epstein, 1999; Guntzer, Keller, & Meunier, 2012; Haynes, 2014; Liang et al., 2007, 2015; Ma, 2004; Ma & Takahashi, 2002; Qian et al., 2019; Savant et al., 1996; Zama et al., 2018), decreasing their bioavailability to plant roots.

The mechanisms of Si-mediated alleviation of Al toxicity involves Al adsorption on Si–O sites, formation of Si–O–Al–O–Si bonds and coprecipitation as hydroxy-aluminosilicate (HAS) complexes (Cooke & Leishman, 2016; Corrales, Poschenrieder, & Barceló, 1997; Hodson & Evans, 1995; Liang et al., 2007). Supplying phytolith biochar may thus alleviate Al toxicity through HAS coprecipitation (Qian et al., 2016). The alleviation of Al toxicity in acid soils is further enhanced through the liming effect of biochar (Hodson & Evans, 1995; Hodson & Sangster, 1993; Liang et al., 2007; Mossor-Pietraszewska, 2001; Qian, Chen, & Hu, 2013), and Al complexation by pyrolyzed organic substances (Mimmo, Marzadori, Montecchio, & Gessa, 2005; Qian & Chen, 2013; Xia & Rayson, 1998).

5.3 | Biochar increases plant biomass and crop yield

Crop biochar application significantly increases plant biomass and crop yield (Jeffery et al., 2011). This impact is, however, much larger for plant biomass than for crop yield (Jeffery et al., 2011), and more significant in pot experiments than in field trials (Cross & Sohi, 2011; Dong et al., 2013; Haefele et al., 2011; Peng, Ye, Wang, Zhou, & Sun, 2011; Schulz & Glaser, 2012; Sohi et al., 2010; Uzoma et al., 2011; Windeatt et al., 2014; Yuan, Xu, & Qian, 2011; Zhang et al., 2012). As discussed above, this impact is explained by the improvement in soil fertility and the mitigation of abiotic and biotic stresses. In particular, biochar supply boosts nutrient cycles. The nutrients concerned are carbon (Gaunt & Lehmann, 2008; Hagemann et al., 2017; Jeffery et al., 2015; Lehmann et al., 2006; Lehmann & Joseph, 2015), nitrogen (Clough & Condron, 2010; Rondon, Lehmann, Ramírez, & Hurtado, 2007; Saarnio, Heimonen, & Kettunen, 2013; Tan, Ye, Zhang, & Huang, 2018), phosphorus (Chan & Xu, 2009; Dai et al., 2016; Madiba, Solaiman, Carson, & Murphy, 2016; Van Zwieten et al., 2010; Vanek & Lehmann, 2015), as well as K, Ca, Na, and Mg (Hardy et al., 2016; Joseph et al., 2010; Kloss et al., 2014; Laird et al., 2010; Li, Song, et al., 2019; Macdonald, Farrell, Zwieten, & Krull, 2014; Sohi et al., 2010; Van Zwieten et al., 2010).

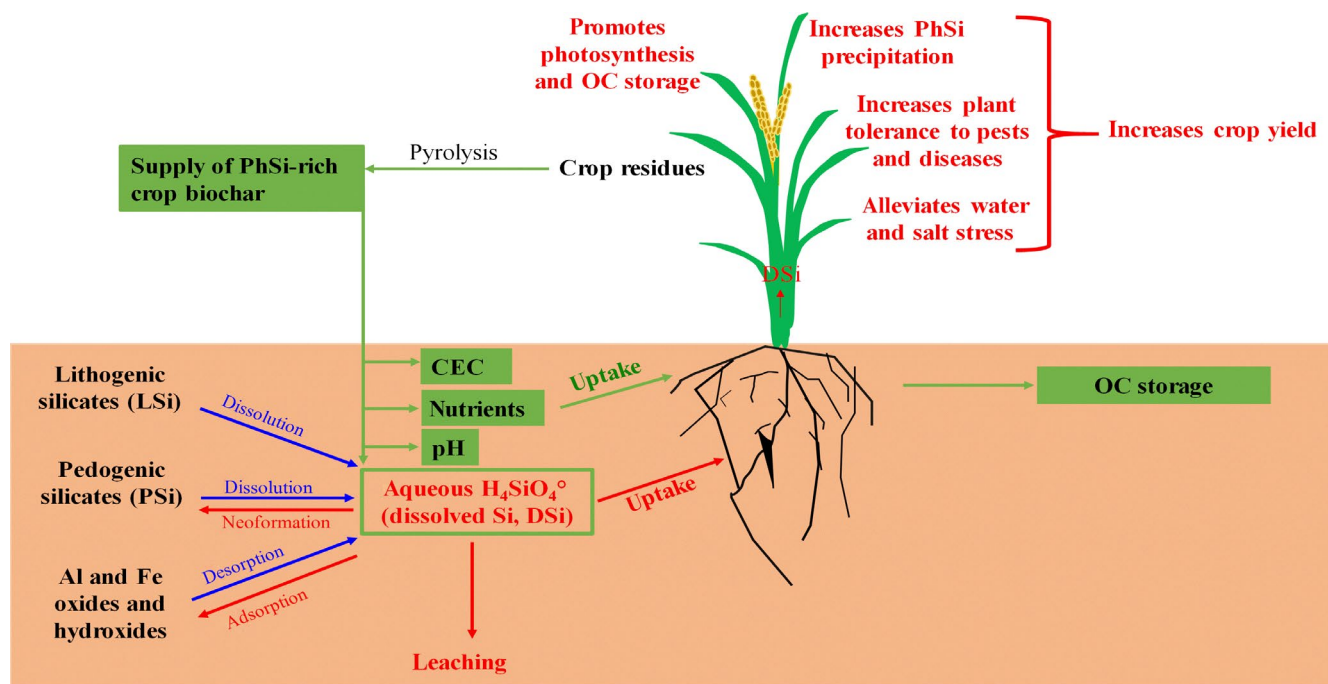


FIGURE 8 Schematic overview of the potential effects of PhSi-rich biochar supply in croplands

5.4 | PhSi biochar boosts the biological Si feedback loop

The present review demonstrates the potential of phytolith biochar to boost the biological Si feedback loop of the soil–plant cycle in agroecosystems (Figure 2). The basic principles to achieve this boost are to maximize the restitution of PhSi-bearing biochars to cultivated soils, and to optimize the conditions promoting the release of plant-available Si in the soil–plant system. These conditions are linked to soil properties such as pH as well as soil processes such as i.a. acid buffering, and DSi adsorption onto oxide surfaces, and bio-silicification. Boosting the biological Si feedback loop of the soil–plant cycle (Figure 2) in agroecosystems through phytolith biochar supply is expected to be particularly efficient in highly weathered soils. Given the global estimates of available PhSi biochar and the surface covered by highly weathered soils in the tropics (Ferralsols, Acrisols, Lixisols, Nitisols), we tentatively estimate a global rate of biochar application of $1.7 \text{ ha}^{-1} \text{ year}^{-1}$. This global estimation is, of course, theoretical, since it supposes free access to PhSi biochars and free circulation of this material.

6 | CONCLUSION

The pyrolysis of crop straws or residues from Si-accumulating plants provides biochars contributing to feed the reservoirs of stable carbon and plant-available Si in agroecosystems. Feedstock type, pyrolysis temperature, soil pH,

soil properties and processes are the main factors that exert a decisive control on the supply of plant-available Si and other benefits (Figure 8). The expected improvement is especially meaningful for highly weathered soils intensively used for cropping Si high-accumulator plants. On a global scale, ample amounts of feedstocks for phytolith biochar are available. The largest benefits can be expected under the following conditions: (a) the use of cereals (rice, wheat, maize) and sugarcane crop residues as feedstock materials; (b) pyrolytic process performed slowly up to $350\text{--}500^\circ\text{C}$ for tree or wood biochar, $500\text{--}600^\circ\text{C}$ for crop biochar, but not above 700°C to prevent silica crystallization; (c) an optimal liming effect increasing soil pH to release plant-available Si.

World agriculture faces multiple challenges due to current high demands in food and environmental concerns. Quantifications about the cost and benefits should be compared between phytolith biochar and traditional Si fertilizers. The analysis should take into account both the agronomic (e.g., crop yield) and environmental aspects (e.g., sustainable ecosystem development) induced by Si ecological services. The supply of phytolith biochar indeed positively affects the reservoir of plant-available Si and other nutrients, stable OC, as well as soil fertility, given the ample Si ecosystem services offered by biochars.

ACKNOWLEDGEMENTS

Z. Li is supported by the 'Fonds Spécial de Recherche' of the UCL in 2014–2015 and the Aspirant (ASP)-'Fonds National de la Recherche Scientifique' (FNRS) of Belgium (FC49049).

AUTHORS' CONTRIBUTIONS

Both authors contributed to paper writing and revision.

ORCID

Zimin Li  <https://orcid.org/0000-0002-6377-2636>

REFERENCES

- Abbas, T., Rizwan, M., Ali, S., Zia-ur-Rehman, M., Farooq Qayyum, M., Abbas, F., ... Sik Ok, Y. (2017). Effect of biochar on cadmium bioavailability and uptake in wheat (*Triticum aestivum* L.) grown in a soil with aged contamination. *Ecotoxicology and Environmental Safety*, 140, 37–47. <https://doi.org/10.1016/j.ecoenv.2017.02.028>
- Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., ... Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, 99, 19–33. <https://doi.org/10.1016/j.chemosphere.2013.10.071>
- Alexandre, A., Meunier, J.-D., Colin, F., & Koud, J.-M. (1997). Plant impact on the biogeochemical cycle of silicon and related weathering processes. *Geochimica et Cosmochimica Acta*, 61, 677–682. [https://doi.org/10.1016/S0016-7037\(97\)00001-X](https://doi.org/10.1016/S0016-7037(97)00001-X)
- Ali, S., Rizwan, M., Qayyum, M. F., Ok, Y. S., Ibrahim, M., Riaz, M., ... Shahzad, A. N. (2017). Biochar soil amendment on alleviation of drought and salt stress in plants: A critical review. *Environmental Science and Pollution Research International*, 24, 12700–12712. <https://doi.org/10.1007/s11356-017-8904-x>
- Atkinson, C. J., Fitzgerald, J. D., & Higgs, N. A. (2010). Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review. *Plant and Soil*, 337, 1–18. <https://doi.org/10.1007/s11104-010-0464-5>
- Barão, L., Clymans, W., Vandevenne, F., Meire, P., Conley, D., & Struyf, E. (2014). Pedogenic and biogenic alkaline-extracted silicon distributions along a temperate land-use gradient. *European Journal of Soil Science*, 65, 693–705. <https://doi.org/10.1111/ejss.12161>
- Bartoli, F. (1983). The biogeochemical cycle of silicon in two temperate forest ecosystems. *Ecological Bulletins*, 469–476.
- Bartoli, F. (1985). Crystallochemistry and surface properties of biogenic opal. *European Journal of Soil Science*, 36, 335–350. <https://doi.org/10.1111/j.1365-2389.1985.tb00340.x>
- Bartoli, F., & Wilding, L. (1980). Dissolution of biogenic opal as a function of its physical and chemical properties. *Soil Science Society of America Journal*, 44, 873–878. <https://doi.org/10.2136/sssaj1980.03615995004400040043x>
- Beesley, L., & Marmiroli, M. (2011). The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environmental Pollution*, 159, 474–480. <https://doi.org/10.1016/j.envpol.2010.10.016>
- Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., & Sizmur, T. (2011). A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental Pollution*, 159, 3269–3282. <https://doi.org/10.1016/j.envpol.2011.07.023>
- Belanger, R. R. (1995). Soluble silicon: Its role in crop and disease management of greenhouse crops. *Plant Disease*, 79, 329–336. <https://doi.org/10.1094/PD-79-0329>
- Berthelsen, S., Noble, A., & Garside, A. (2001). Silicon research down under: Past, present, and future. *Studies in Plant Science*, 8, 241–255. [https://doi.org/10.1016/S0928-3420\(01\)80019-7](https://doi.org/10.1016/S0928-3420(01)80019-7)
- Bettermann, P., & Liebau, F. (1975). The transformation of amorphous silica to crystalline silica under hydrothermal conditions. *Contributions to Mineralogy and Petrology*, 53, 25–36. <https://doi.org/10.1007/BF00402452>
- Biederman, L. A., & Harpole, W. S. (2013). Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *GCB Bioenergy*, 5, 202–214. <https://doi.org/10.1111/gcbb.12037>
- Blecker, S. W., McCulley, R. L., Chadwick, O. A., & Kelly, E. F. (2006). Biologic cycling of silica across a grassland bioclimosequence. *Global Biogeochemical Cycles*, 20. <https://doi.org/10.1029/2006GB002690>
- Boateng, A. A., Garcia-Perez, M., Mašek, O., Brown, R., & DelCampo, B. (2015). Biochar production technology. In J. Lehmann & S. Joseph (Eds.), *Biochar for environmental management: Science and technology* (2nd edn.) (pp. 64–89). London: Routledge, Earthscan Books Ltd.
- Brady, P. V., & Walther, J. V. (1990). Kinetics of quartz dissolution at low temperatures. *Chemical Geology*, 82, 253–264. [https://doi.org/10.1016/0009-2541\(90\)90084-K](https://doi.org/10.1016/0009-2541(90)90084-K)
- Cabanes, D., Weiner, S., & Shahack-Gross, R. (2011). Stability of phytoliths in the archaeological record: A dissolution study of modern and fossil phytoliths. *Journal of Archaeological Science*, 38, 2480–2490. <https://doi.org/10.1016/j.jas.2011.05.020>
- Carey, J. C., & Fulweiler, R. W. (2012). The terrestrial silica pump. *PLoS ONE*, 7, e52932. <https://doi.org/10.1371/journal.pone.0052932>
- ICermeño, P., Falkowski, P. G., Romero, O. E., Schaller, M. F., & Vallina, S. M. (2015). Continental erosion and the Cenozoic rise of marine diatoms. *Proceedings of the National Academy of Sciences of the United States of America*, 112, 4239–4244. <https://doi.org/10.1073/pnas.1412883112>
- Chan, K. Y., & Xu, Z. (2009). Biochar: Nutrient properties and their enhancement. *Biochar for Environmental Management: Science and Technology*, 1, 67–84.
- Chia, C. H., Downie, A., & Munroe, P. (2015). Characteristics of biochar: Physical and structural properties. In J. Lehmann & S. Joseph (Eds.), *Biochar for environmental management: Science and technology* (2nd edn., pp. 89–109). London: Routledge, Earthscan Books Ltd.
- Clough, T. J., & Condron, L. M. (2010). Biochar and the nitrogen cycle: Introduction. *Journal of Environmental Quality*, 39, 1218–1223. <https://doi.org/10.2134/jeq2010.0204>
- Clymans, W., Struyf, E., Govers, G., Vandevenne, F., & Conley, D. (2011). Anthropogenic impact on amorphous silica pools in temperate soils. *Biogeosciences*, 8, 2281–2293. <https://doi.org/10.5194/bg-8-2281-2011>
- Conley, D. J. (2002). Terrestrial ecosystems and the global biogeochemical silica cycle. *Global Biogeochemical Cycles*, 16, 68–168. <https://doi.org/10.1029/2002GB001894>
- Conley, D. J., & Carey, J. C. (2015). Biogeochemistry: Silica cycling over geologic time. *Nature Geoscience*, 8, 431–432. <https://doi.org/10.1038/ngeo2454>
- Conley, D. J., Likens, G. E., Buso, D. C., Saccone, L., Bailey, S. W., & Johnson, C. E. (2008). Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest. *Global Change Biology*, 14, 2548–2554. <https://doi.org/10.1111/j.1365-2486.2008.01667.x>
- Cooke, J., Degabriel, J. L., & Hartley, S. E. (2016). The functional ecology of plant silicon: Geoscience to genes. *Functional Ecology*, 30, 1270–1276. <https://doi.org/10.1111/1365-2435.12711>

- Cooke, J., & Leishman, M. R. (2016). Consistent alleviation of abiotic stress with silicon addition: A meta-analysis. *Functional Ecology*, 30, 1340–1357. <https://doi.org/10.1111/1365-2435.12713>
- Cornelis, J. T., & Delvaux, B. (2016). Soil processes drive the biological silicon feedback loop. *Functional Ecology*, 30(8), 1298–1310.
- Corrales, I., Poschenrieder, C., & Barceló, J. (1997). Influence of silicon pretreatment on aluminium toxicity in maize roots. *Plant and Soil*, 190, 203–209.
- Coskun, D., Deshmukh, R., Sonah, H., Menzies, J. G., Reynolds, O., Ma, J. F., ... Bélanger, R. R. (2019). The controversies of silicon's role in plant biology. *New Phytologist*, 221, 67–85. <https://doi.org/10.1111/nph.15343>
- Crane-Droesch, A., Abiven, S., Jeffery, S., & Torn, M. S. (2013). Heterogeneous global crop yield response to biochar: A meta-regression analysis. *Environmental Research Letters*, 8, 044049. <https://doi.org/10.1088/1748-9326/8/4/044049>
- Cross, A., & Sohi, S. P. (2011). The priming potential of biochar products in relation to labile carbon contents and soil organic matter status. *Soil Biology and Biochemistry*, 43, 2127–2134. <https://doi.org/10.1016/j.soilbio.2011.06.016>
- Dai, L., Li, H., Tan, F., Zhu, N., He, M., & Hu, G. (2016). Biochar: A potential route for recycling of phosphorus in agricultural residues. *GCB Bioenergy*, 8, 852–858. <https://doi.org/10.1111/gcbb.12365>
- Datnoff, L. E., & Heckman, J. R. (2014). Silicon fertilizers for plant disease protection. In *16th World Fertilizer Congress of CIEC*. Rio de Janeiro, Brazil.
- Datnoff, L. E., Snyder, G. H., & Korndörfer, G. H. (2001). *Silicon in agriculture*. Amsterdam, the Netherlands: Elsevier.
- Demirbas, A. (2004). Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *Journal of Analytical Applied Pyrolysis*, 72, 243–248. <https://doi.org/10.1016/j.jaap.2004.07.003>
- Deshmukh, R., & Bélanger, R. R. (2016). Molecular evolution of aquaporins and silicon influx in plants. *Functional Ecology*, 30, 1277–1285. <https://doi.org/10.1111/1365-2435.12570>
- Desplanques, V., Cary, L., Mouret, J.-C., Trolard, F., Bourrié, G., Grauby, O., & Meunier, J.-D. (2006). Silicon transfers in a rice field in Camargue (France). *Journal of Geochemical Exploration*, 88, 190–193. <https://doi.org/10.1016/j.gexplo.2005.08.036>
- Dong, D., Yang, M., Wang, C., Wang, H., Li, Y., Luo, J., & Wu, W. (2013). Responses of methane emissions and rice yield to applications of biochar and straw in a paddy field. *Journal of Soils and Sediments*, 13, 1450–1460. <https://doi.org/10.1007/s11368-013-0732-0>
- Dove, P. (1995). Kinetic and thermodynamic controls on silica reactivity in weathering environments. *Reviews in Mineralogy and Geochemistry*, 31, 235–290. <https://doi.org/10.1515/9781501509650-008>
- Dove, P. M., & Elston, S. F. (1992). Dissolution kinetics of quartz in sodium chloride solutions: Analysis of existing data and a rate model for 25°C. *Geochimica et Cosmochimica Acta*, 56, 4147–4156. [https://doi.org/10.1016/0016-7037\(92\)90257-J](https://doi.org/10.1016/0016-7037(92)90257-J)
- Driessen, P., Deckers, J., Spaargaren, O., & Nachtergaele, F. (2000). *Lecture notes on the major soils of the world*. Rome, Italy: Food and Agriculture Organization (FAO).
- Elbaum, R., Weiner, S., Albert, R. M., & Elbaum, M. (2003). Detection of burning of plant materials in the archaeological record by changes in the refractive indices of siliceous phytoliths. *Journal of Archaeological Science*, 30, 217–226. <https://doi.org/10.1006/jasc.2002.0828>
- Epstein, E. (1999). Silicon. *Annual Review of Plant Physiology and Plant Molecular Biology*, 50, 641–664. <https://doi.org/10.1146/annurev.arplant.50.1.641>
- Epstein, E. (2001). Silicon in plants: Facts vs. concepts. *Studies in Plant Science*, 8, 1–15. [https://doi.org/10.1016/S0928-3420\(01\)80005-7](https://doi.org/10.1016/S0928-3420(01)80005-7)
- Exley, C. (2015). A possible mechanism of biological silicification in plants. *Frontiers in Plant Science*, 6, 853. <https://doi.org/10.3389/fpls.2015.00853>
- Farmer, V., Delbos, E., & Miller, J. J. G. (2005). The role of phytolith formation and dissolution in controlling concentrations of silica in soil solutions and streams. *Geoderma*, 127, 71–79. <https://doi.org/10.1016/j.geoderma.2004.11.014>
- Fauteux, F., Rémus-Borel, W., Menzies, J. G., & Bélanger, R. R. (2005). Silicon and plant disease resistance against pathogenic fungi. *FEMS Microbiology Letters*, 249, 1–6. <https://doi.org/10.1016/j.femsle.2005.06.034>
- Frayse, F., Pokrovsky, O. S., Schott, J., & Meunier, J.-D. (2006). Surface properties, solubility and dissolution kinetics of bamboo phytoliths. *Geochimica et Cosmochimica Acta*, 70, 1939–1951. <https://doi.org/10.1016/j.gca.2005.12.025>
- Frayse, F., Pokrovsky, O. S., Schott, J., & Meunier, J.-D. (2009). Surface chemistry and reactivity of plant phytoliths in aqueous solutions. *Chemical Geology*, 258, 197–206. <https://doi.org/10.1016/j.chemgeo.2008.10.003>
- Gascho, G. J. (2001). Silicon sources for agriculture. *Studies in Plant Science*, 8, 197–207. [https://doi.org/10.1016/S0928-3420\(01\)80016-1](https://doi.org/10.1016/S0928-3420(01)80016-1)
- Gaunt, J. L., & Lehmann, J. (2008). Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. *Environmental Science and Technology*, 42, 4152–4158. <https://doi.org/10.1021/es071361i>
- Glaser, B., & Woods, W. I. (2004). *Amazonian dark earths: Explorations in space and time*. Berlin: Springer.
- Guntzer, F., Keller, C., & Meunier, J.-D. (2012). Benefits of plant silicon for crops: A review. *Agronomy for Sustainable Development*, 32, 201–213. <https://doi.org/10.1007/s13593-011-0039-8>
- Guntzer, F., Keller, C., Poulton, P. R., Mcgrath, S. P., & Meunier, J.-D. (2012). Long-term removal of wheat straw decreases soil amorphous silica at Broadbalk, Rothamsted. *Plant and Soil*, 352, 173–184. <https://doi.org/10.1007/s11104-011-0987-4>
- Guo, F., Song, Z., Sullivan, L., Wang, H., Liu, X., Wang, X., ... Zhao, Y. (2015). Enhancing phytolith carbon sequestration in rice ecosystems through basalt powder amendment. *Science Bulletin*, 60, 591–597. <https://doi.org/10.1007/s11434-015-0729-8>
- Guo, J., & Chen, B. (2014). Insights on the molecular mechanism for the recalcitrance of biochars: Interactive effects of carbon and silicon components. *Environmental Science & Technology*, 48, 9103–9112. <https://doi.org/10.1021/es405647e>
- Haefele, S., Konboon, Y., Wongboon, W., Amarante, S., Maarifat, A., Pfeiffer, E., & Knoblauch, C. (2011). Effects and fate of biochar from rice residues in rice-based systems. *Field Crops Research*, 121, 430–440. <https://doi.org/10.1016/j.fcr.2011.01.014>
- Hagemann, N., Joseph, S., Schmidt, H.-P., Kammann, C. I., Harter, J., Borch, T., ... Kappler, A. (2017). Organic coating on biochar explains its nutrient retention and stimulation of soil fertility. *Nature Communications*, 8, 1089. <https://doi.org/10.1038/s41467-017-01123-0>
- Hardy, B., Cornelis, J. T., Houben, D., Leifeld, J., Lambert, R., & Dufey, J. (2016). Evaluation of the long-term effect of biochar on properties

- of temperate agricultural soil at pre-industrial charcoal kiln sites in Wallonia, Belgium. *European Journal of Soil Science*, 68, 80–89. <https://doi.org/10.1111/ejss.12395>
- Hartley, S. E., & Degabriel, J. L. (2016). The ecology of herbivore-induced silicon defences in grasses. *Functional Ecology*, 30, 1311–1322. <https://doi.org/10.1111/1365-2435.12706>
- Haynes, R. J. (2014). A contemporary overview of silicon availability in agricultural soils. *Journal of Plant Nutrition and Soil Science*, 177, 831–844. <https://doi.org/10.1002/jpln.201400202>
- Haynes, R. J. (2017). Significance and role of Si in crop production. *Advances in Agronomy*, 146, 83–166. <https://doi.org/10.1016/bs.agron.2017.06.001>
- Haynes, R. J., Belyaeva, O. N., & Kingston, G. (2013). Evaluation of industrial wastes as sources of fertilizer silicon using chemical extractions and plant uptake. *Journal of Plant Nutrition and Soil Science*, 176, 238–248. <https://doi.org/10.1002/jpln.201200372>
- Haynes, R. J., & Zhou, Y.-F. (2018). Effect of pH and added slag on the extractability of Si in two Si-deficient sugarcane soils. *Chemosphere*, 193, 431–437. <https://doi.org/10.1016/j.chemosphere.2017.10.175>
- Henriet, C., Bodarwé, L., Dorel, M., Draye, X., & Delvaux, B. (2008). Leaf silicon content in banana (*Musa* spp.) reveals the weathering stage of volcanic ash soils in Guadeloupe. *Plant and Soil*, 313, 71–82. <https://doi.org/10.1007/s11104-008-9680-7>
- Hodson, M. J., & Evans, D. E. (1995). Aluminium/silicon interactions in higher plants. *Journal of Experimental Botany*, 46, 161–171. <https://doi.org/10.1093/jxb/46.2.161>
- Hodson, M., & Sangster, A. (1993). The interaction between silicon and aluminium in *Sorghum bicolor* (L.) Moench: Growth analysis and X-ray microanalysis. *Annals of Botany*, 72, 389–400. <https://doi.org/10.1006/anbo.1993.1124>
- Hodson, M., White, P. J., Mead, A., & Broadley, M. (2005). Phylogenetic variation in the silicon composition of plants. *Annals of Botany*, 96, 1027–1046. <https://doi.org/10.1093/aob/mci255>
- Hoogwijk, M., Faaij, A., Van Den Broek, R., Berndes, G., Gielen, D., & Turkenburg, W. (2003). Exploration of the ranges of the global potential of biomass for energy. *Biomass and Bioenergy*, 25, 119–133. [https://doi.org/10.1016/S0961-9534\(02\)00191-5](https://doi.org/10.1016/S0961-9534(02)00191-5)
- Houben, D., Evrard, L., & Sonnet, P. (2013). Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. *Chemosphere*, 92, 1450–1457. <https://doi.org/10.1016/j.chemosphere.2013.03.055>
- Houben, D., Sonnet, P., & Cornelis, J.-T. (2014). Biochar from *Miscanthus*: A potential silicon fertilizer. *Plant and Soil*, 374, 871–882. <https://doi.org/10.1007/s11104-013-1885-8>
- Iler, R. K. (1979). *Chemistry of silica-solubility, polymerization, colloid and surface properties and biochemistry*. New York, NY: Wiley.
- Inyang, M. I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., ... Cao, X. (2016). A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. *Critical Reviews in Environmental Science Technology*, 46, 406–433. <https://doi.org/10.1080/10643389.2015.1096880>
- Ippolito, J. A., Spokas, K. A., Novak, J. M., Lentz, R. D., & Cantrell, K. B. (2015). Biochar elemental composition and factors influencing nutrient retention. In J. Lehmann & S. Joseph (Eds.), *Biochar for environmental management: Science, technology and implementation* (pp. 139–163). London: Routledge, Earthscan Books Ltd..
- IUSS. (2014). *World reference base for soil resources 2014 international soil classification system for naming soils and creating legends for soil maps*. Rome: FAO.
- Jeffery, S., Bezemer, T. M., Cornelissen, G., Kuyper, T. W., Lehmann, J., Mommer, L., ... van Groenigen, J. W. (2015). The way forward in biochar research: Targeting trade-offs between the potential wins. *GCB Bioenergy*, 7, 1–13. <https://doi.org/10.1111/gcbb.12132>
- Jeffery, S., Verheijen, F. G., Van Der Velde, M., & Bastos, A. C. (2011). A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agriculture, Ecosystems & Environment*, 144, 175–187. <https://doi.org/10.1016/j.agee.2011.08.015>
- Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. A., & Sonoki, T. (2014). Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences*, 11, 6613–6621. <https://doi.org/10.5194/bg-11-6613-2014>
- Jones, L., & Handreck, K. (1967). Silica in soils, plants, and animals. *Advances in Agronomy*, 19, 107–149. [https://doi.org/10.1016/s0065-2113\(08\)60734-8](https://doi.org/10.1016/s0065-2113(08)60734-8)
- Jones, L., & Milne, A. A. (1963). Studies of silica in the oat plant: I. Chemical and physical properties of the silica. *Plant and Soil*, 18, 207–220. <https://doi.org/10.1007/BF01347875>
- Joseph, S. D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., ... Amonette, J. E. (2010). An investigation into the reactions of biochar in soil. *Soil Research*, 48, 501–515. <https://doi.org/10.1071/SR10009>
- Keeping, M. G. (2017). Uptake of silicon by sugarcane from applied sources may not reflect plant-available soil silicon and total silicon content of sources. *Frontiers in Plant Science*, 8, 760. <https://doi.org/10.3389/fpls.2017.00760>
- Keller, C., Guntzer, F., Barboni, D., Labreuche, J., & Meunier, J.-D. (2012). Impact of agriculture on the Si biogeochemical cycle: Input from phytolith studies. *Comptes Rendus Geoscience*, 344, 739–746. <https://doi.org/10.1016/j.crte.2012.10.004>
- Kelly, E. (1990). Methods for extracting opal phytoliths from soil and plant material. In *Workshop on biotic indicators of global change*. Seattle, WA: University of Washington.
- Kloss, S., Zehetner, F., Wimmer, B., Buecker, J., Rempt, F., & Soja, G. (2014). Biochar application to temperate soils: Effects on soil fertility and crop growth under greenhouse conditions. *Journal of Plant Nutrition and Soil Science*, 177, 3–15. <https://doi.org/10.1002/jpln.201200282>
- Klotzbücher, T., Marxen, A., Vetterlein, D., Schneiker, J., Türke, M., van Sinh, N., ... Jahn, R. (2015). Plant-available silicon in paddy soils as a key factor for sustainable rice production in Southeast Asia. *Basic and Applied Ecology*, 16, 665–673. <https://doi.org/10.1016/j.baae.2014.08.002>
- Krishnan, S., Samson, N., Ravichandran, P., Narasimhan, D., & Dayanandan, P. (2000). Phytoliths of Indian grasses and their potential use in identification. *Botanical Journal of the Linnean Society*, 132, 241–252. <https://doi.org/10.1111/j.1095-8339.2000.tb01529.x>
- Lahr, D. J., Bosak, T., Lara, E., & Mitchell, E. A. (2015). The Phanerozoic diversification of silica-cycling testate amoebae and its possible links to changes in terrestrial ecosystems. *PeerJ*, 3, e1234. <https://doi.org/10.7717/peerj.1234>
- Laird, D. A., Fleming, P., Davis, D. D., Horton, R., Wang, B., & Karlen, D. L. (2010). Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma*, 158, 443–449. <https://doi.org/10.1016/j.geoderma.2010.05.013>
- Lal, R. (2005). World crop residues production and implications of its use as a biofuel. *Environment International*, 31, 575–584. <https://doi.org/10.1016/j.envint.2004.09.005>

- Lehmann, J. (2007). A handful of carbon. *Nature*, 447, 143–144. <https://doi.org/10.1038/447143a>
- Lehmann, J., Da Silva Jr, J. P., Steiner, C., Nehls, T., Zech, W., & Glaser, B. (2003). Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: Fertilizer, manure and charcoal amendments. *Plant and Soil*, 249, 343–357.
- Lehmann, J., Gaunt, J., & Rondon, M. (2006). Bio-char sequestration in terrestrial ecosystems – A review. *Mitigation Adaptation Strategies for Global Change*, 11, 403–427. <https://doi.org/10.1007/s11027-005-9006-5>
- Lehmann, J., & Joseph, S. (2015). Biochar for environmental management: An introduction. In J. Lehmann & S. Joseph (Eds.), *Biochar for environmental management: Science, technology and implementation* (pp. 1–13). London: Routledge.
- Li, D. D., Lerman, A., & Mackenzie, F. T. (2011). Human perturbations on the global biogeochemical cycles of coupled Si–C and responses of terrestrial processes and the coastal ocean. *Applied Geochemistry*, 26, S289–S291. <https://doi.org/10.1016/j.apgeochem.2011.03.084>
- Li, Z., Delvaux, B., Yans, J., Dufour, N., Houben, D., & Cornelis, J.-T. (2018). Phytolith-rich biochar increases cotton biomass and silicon-mineralomass in a highly weathered soil. *Journal of Plant Nutrition and Soil Science*, 181, 537–546. <https://doi.org/10.1002/jpln.201800031>
- Li, Z., Song, Z., & Cornelis, J.-T. (2014). Impact of rice cultivar and organ on elemental composition of phytoliths and the release of bio-available silicon. *Frontiers in Plant Science*, 5, <https://doi.org/10.3389/fpls.2014.00529>
- Li, Z., Song, Z., Singh, B. P., & Wang, H. (2019). The impact of crop residue biochars on silicon and nutrient cycles in croplands. *Science of the Total Environment*, 659, 673–680. <https://doi.org/10.1016/j.scitotenv.2018.12.381>
- Li, Z., Unzué-Belmonte, D., Cornelis, J.-T., Linden, C. V., Struyf, E., Ronsse, F., & Delvaux, B. (2019). Effects of phytolithic rice-straw biochar, soil buffering capacity and pH on silicon bioavailability. *Plant and Soil*, 438, 187–203. <https://doi.org/10.1007/s11104-019-04013-0>
- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., ... Neves, E. G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal*, 70, 1719–1730. <https://doi.org/10.2136/sssaj2005.0383>
- Liang, Y. C., Ma, T. S., Li, F. J., & Feng, Y. J. (1994). Silicon availability and response of rice and wheat to silicon in calcareous soils. *Communications in Soil Science & Plant Analysis*, 25, 2285–2297. <https://doi.org/10.1080/00103629409369189>
- Liang, Y., Nikolic, M., Bélanger, R., Gong, H., & Song, A. (2015). *Silicon in agriculture: From theory to practice*. Dordrecht, the Netherlands: Springer.
- Liang, Y., Si, J., & Römhild, V. (2005). Silicon uptake and transport is an active process in *Cucumis sativus*. *New Phytologist*, 167, 797–804. <https://doi.org/10.1111/j.1469-8137.2005.01463.x>
- Liang, Y., Sun, W., Zhu, Y.-G., & Christie, P. (2007). Mechanisms of silicon-mediated alleviation of abiotic stresses in higher plants: A review. *Environmental Pollution*, 147, 422–428. <https://doi.org/10.1016/j.envpol.2006.06.008>
- Liu, X., Li, L., Bian, R., Chen, D. E., Qu, J., Wanjiru Kibue, G., ... Zheng, J. (2014). Effect of biochar amendment on soil-silicon availability and rice uptake. *Journal of Plant Nutrition and Soil Science*, 177, 91–96. <https://doi.org/10.1002/jpln.201200582>
- Liu, X., Zhang, A., Ji, C., Joseph, S., Bian, R., Li, L., ... Paz-Ferreiro, J. (2013). Biochar's effect on crop productivity and the dependence on experimental conditions—A meta-analysis of literature data. *Plant and Soil*, 373, 583–594. <https://doi.org/10.1007/s11104-013-1806-x>
- Lu, K., Yang, X., Gielen, G., Bolan, N., Ok, Y. S., Niazi, N. K., ... Wang, H. (2017). Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. *Journal of Environmental Management*, 186, 285–292. <https://doi.org/10.1016/j.jenvman.2016.05.068>
- Lucas, Y., Luizao, F. J., Chauvel, A., Rouiller, J., & Nahon, D. (1993). The relation between biological activity of the rain forest and mineral composition of soils. *Science*, 260, 521–523. <https://doi.org/10.1126/science.260.5107.521>
- Ma, J. F. (2004). Role of silicon in enhancing the resistance of plants to biotic and abiotic stresses. *Soil Science and Plant Nutrition*, 50, 11–18. <https://doi.org/10.1080/00380768.2004.10408447>
- Ma, J., Miyake, Y., & Takahashi, E. (2001). Silicon as a beneficial element for crop plants. *Studies in Plant Science*, 8, 17–39. [https://doi.org/10.1016/s0928-3420\(01\)80006-9](https://doi.org/10.1016/s0928-3420(01)80006-9)
- Ma, J. F., & Takahashi, E. (2002). *Soil, fertilizer, and plant silicon research in Japan*. Amsterdam, the Netherlands: Elsevier.
- Ma, J. F., Tamai, K., Yamaji, N., Mitani, N., Konishi, S., Katsuhara, M., ... Yano, M. (2006). A silicon transporter in rice. *Nature*, 440, 688–691. <https://doi.org/10.1038/nature04590>
- Ma, J. F., & Yamaji, N. (2008). Functions and transport of silicon in plants. *Cellular and Molecular Life Sciences*, 65, 3049–3057. <https://doi.org/10.1007/s00018-008-7580-x>
- Ma, J. F., Yamaji, N., Mitani, N., Tamai, K., Konishi, S., Fujiwara, T., ... Yano, M. (2007). An efflux transporter of silicon in rice. *Nature*, 448, 209–212. <https://doi.org/10.1038/nature05964>
- Macdonald, L. M., Farrell, M., Van Zwieten, L., & Krull, E. S. (2014). Plant growth responses to biochar addition: An Australian soils perspective. *Biology and Fertility of Soils*, 50, 1035–1045. <https://doi.org/10.1007/s00374-014-0921-z>
- Madiba, O. F., Solaiman, Z. M., Carson, J. K., & Murphy, D. V. (2016). Biochar increases availability and uptake of phosphorus to wheat under leaching conditions. *Biology Fertility of Soils*, 52, 439–446. <https://doi.org/10.1007/s00374-016-1099-3>
- Marxen, A., Klotzbücher, T., Jahn, R., Kaiser, K., Nguyen, V. S., Schmidt, A., ... Vetterlein, D. (2016). Interaction between silicon cycling and straw decomposition in a silicon deficient rice production system. *Plant and Soil*, 398, 153–163. <https://doi.org/10.1007/s11104-015-2645-8>
- Mckeague, J., & Cline, M. (1963). Silica in soils. *Advances in Agronomy*, 15, 339–396. [https://doi.org/10.1016/s0065-2113\(08\)60403-4](https://doi.org/10.1016/s0065-2113(08)60403-4)
- Meunier, J. D., Barboni, D., Anwar-ul-Haq, M., Levard, C., Chaurand, P., Vidal, V., ... Keller, C. (2017). Effect of phytoliths for mitigating water stress in durum wheat. *New Phytologist*, 215, 229–239. <https://doi.org/10.1111/nph.14554>
- Meunier, J., Colin, F., & Alarcon, C. (1999). Biogenic silica storage in soils. *Geology*, 27, 835–838. [https://doi.org/10.1130/0091-7613\(1999\)027<0835:BSSIS>2.3.CO;2](https://doi.org/10.1130/0091-7613(1999)027<0835:BSSIS>2.3.CO;2)
- Meunier, J., Guntzer, F., Kirman, S., & Keller, C. (2008). Terrestrial plant-Si and environmental changes. *Mineralogical Magazine*, 72, 263–267. <https://doi.org/10.1180/minmag.2008.072.1.263>
- Meunier, J.-D., Sandhya, K., Prakash, N. B., Borschneck, D., & Dussouillez, P. (2018). pH as a proxy for estimating plant-available Si? A case study in rice fields in Karnataka (South India). *Plant and Soil*, 432, 143–155. <https://doi.org/10.1007/s11104-018-3758-7>
- Meyer, J., & Keeping, M. (2001). Past, present and future research of the role of silicon for sugarcane in southern Africa.

- Studies in Plant Science*, 8, 257–275. [https://doi.org/10.1016/s0928-3420\(01\)80020-3](https://doi.org/10.1016/s0928-3420(01)80020-3)
- Mimmo, T., Marzadori, C., Montecchio, D., & Gessa, C. (2005). Characterisation of Ca- and Al-pectate gels by thermal analysis and FT-IR spectroscopy. *Carbohydrate Research*, 340, 2510–2519. <https://doi.org/10.1016/j.carres.2005.08.011>
- Mitani, N., & Ma, J. F. (2005). Uptake system of silicon in different plant species. *Journal of Experimental Botany*, 56, 1255–1261. <https://doi.org/10.1093/jxb/eri211>
- Mossor-Pietraszkowska, T. (2001). Effect of aluminium on plant growth and metabolism. *Acta Biochimica Polonica*, English edition, 48, 673–686.
- Nguyen, M. N., Dultz, S., & Guggenberger, G. (2014). Effects of pre-treatment and solution chemistry on solubility of rice-straw phytoliths. *Journal of Plant Nutrition Soil Science*, 177, 349–359. <https://doi.org/10.1002/jpln.201300056>
- Nie, C., Yang, X., Niazi, N. K., Xu, X., Wen, Y., Rinklebe, J., ... Wang, H. (2018). Impact of sugarcane bagasse-derived biochar on heavy metal availability and microbial activity: A field study. *Chemosphere*, 200, 274–282. <https://doi.org/10.1016/j.chemosphere.2018.02.134>
- O'Connor, D., Peng, T., Zhang, J., Tsang, D. C. W., Alessi, D. S., Shen, Z., ... Hou, D. (2018). Biochar application for the remediation of heavy metal polluted land: A review of in situ field trials. *Science of the Total Environment*, 619–620, 815–826. <https://doi.org/10.1016/j.scitotenv.2017.11.132>
- Parr, J. F. (2006). Effect of fire on phytolith coloration. *Geoarchaeology*, 21, 171–185. <https://doi.org/10.1002/gea.20102>
- Parr, J. F., Dolic, V., Lancaster, G., & Boyd, W. E. (2001). A microwave digestion method for the extraction of phytoliths from herbarium specimens. *Review of Palaeobotany and Palynology*, 116, 203–212. [https://doi.org/10.1016/S0034-6667\(01\)00089-6](https://doi.org/10.1016/S0034-6667(01)00089-6)
- Parr, J. F., & Sullivan, L. A. (2005). Soil carbon sequestration in phytoliths. *Soil Biology and Biochemistry*, 37, 117–124. <https://doi.org/10.1016/j.soilbio.2004.06.013>
- Peng, X., Ye, L., Wang, C., Zhou, H., & Sun, B. (2011). Temperature- and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. *Soil Tillage Research*, 112, 159–166. <https://doi.org/10.1016/j.still.2011.01.002>
- Piperno, D. R. (2006). *Phytoliths: A comprehensive guide for archaeologists and paleoecologists*. Lanham, MD: Rowman Altamira.
- Piperno, D. R., & Pearsall, D. M. (1998). The silica bodies of tropical American grasses: morphology, taxonomy, and implications for grass systematics and fossil phytolith identification. *Smithsonian Contributions to Botany*, 85, 1–40.
- Puppe, D., Ehrmann, O., Kaczorek, D., Wanner, M., & Sommer, M. (2015). The protozoic Si pool in temperate forest ecosystems—Quantification, abiotic controls and interactions with earthworms. *Geoderma*, 243, 196–204. <https://doi.org/10.1016/j.geoderma.2014.12.018>
- Puppe, D., Höhn, A., Kaczorek, D., Wanner, M., Wehrhan, M., & Sommer, M. (2017). How big is the influence of biogenic silicon pools on short-term changes in water-soluble silicon in soils? Implications from a study of a 10-year-old soil–plant system. *Biogeosciences*, 14, 5239–5252. <https://doi.org/10.5194/bg-14-5239-2017>
- Puppe, D., & Leue, M. (2018). Physicochemical surface properties of different biogenic silicon structures: Results from spectroscopic and microscopic analyses of protistic and phytogenic silica. *Geoderma*, 330, 212–220. <https://doi.org/10.1016/j.geoderma.2018.06.001>
- Puppe, D., & Sommer, M. (2018). Experiments, uptake mechanisms, and functioning of silicon foliar fertilization—A review focusing on maize, rice, and wheat. *Advances in Agronomy*, 152, 1–49. <https://doi.org/10.1016/bs.agron.2018.07.003>
- Qian, L., & Chen, B. (2013). Dual role of biochars as adsorbents for aluminum: The effects of oxygen-containing organic components and the scattering of silicate particles. *Environmental Science & Technology*, 47, 8759–8768. <https://doi.org/10.1021/es401756h>
- Qian, L., Chen, B., & Chen, M. (2016). Novel alleviation mechanisms of aluminum phytotoxicity via released biosilicon from rice straw-derived biochars. *Scientific Reports*, 6. <https://doi.org/10.1038/srep29346>
- Qian, L., Chen, B., & Hu, D. (2013). Effective alleviation of aluminum phytotoxicity by manure-derived biochar. *Environmental Science and Technology*, 47, 2737–2745. <https://doi.org/10.1021/es3047872>
- Qian, L., Shang, X., Zhang, B. O., Zhang, W., Su, A., Chen, Y., ... Chen, M. (2019). Enhanced removal of Cr (VI) by silicon rich biochar-supported nanoscale zero-valent iron. *Chemosphere*, 215, 739–745. <https://doi.org/10.1016/j.chemosphere.2018.10.030>
- Raveendran, K., Ganesh, A., & Khilar, K. C. (1995). Influence of mineral matter on biomass pyrolysis characteristics. *Fuel*, 74, 1812–1822. [https://doi.org/10.1016/0016-2361\(95\)80013-8](https://doi.org/10.1016/0016-2361(95)80013-8)
- Reddy, D. H. K., & Lee, S.-M. (2014). Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal. *Colloids Surfaces A: Physicochemical Engineering Aspects*, 454, 96–103. <https://doi.org/10.1016/j.colsurfa.2014.03.105>
- Reyerson, P. E., Alexandre, A., Harutyunyan, A., Corbinau, R., Martinez De La Torre, H. A., Badeck, F., ... Santos, G. M. (2016). Unambiguous evidence of old soil carbon in grass biosilica particles. *Biogeosciences*, 13, 1269–1286. <https://doi.org/10.5194/bg-13-1269-2016>
- Riotte, J., Meunier, J.-D., Zambardi, T., Audry, S., Barboni, D., Anupama, K., ... Braun, J.-J. (2018). Processes controlling silicon isotopic fractionation in a forested tropical watershed: Mule Hole Critical Zone Observatory (Southern India). *Geochimica et Cosmochimica Acta*, 228, 301–319. <https://doi.org/10.1016/j.gca.2018.02.046>
- Rondon, M. A., Lehmann, J., Ramírez, J., & Hurtado, M. (2007). Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. *Biology and Fertility of Soils*, 43, 699–708. <https://doi.org/10.1007/s00374-006-0152-z>
- Ronsse, F., Van Hecke, S., Dickinson, D., & Prins, W. (2013). Production and characterization of slow pyrolysis biochar: Influence of feedstock type and pyrolysis conditions. *GCB Bioenergy*, 5, 104–115. <https://doi.org/10.1111/gcbb.12018>
- Saarnio, S., Heimonen, K., & Kettunen, R. (2013). Biochar addition indirectly affects N₂O emissions via soil moisture and plant N uptake. *Soil Biology and Biochemistry*, 58, 99–106. <https://doi.org/10.1016/j.soilbio.2012.10.035>
- Sanchez, P. A. (2019). *Properties and management of soils in the tropics*. Cambridge, UK; New York, NY: Cambridge University Press.
- Savant, N., Snyder, G., & Datnoff, L. (1996). Silicon management and sustainable rice production. *Advances in Agronomy*, 58, 151–199. [https://doi.org/10.1016/s0065-2113\(08\)60255-2](https://doi.org/10.1016/s0065-2113(08)60255-2)
- Schlesinger, W. H., & Amundson, R. (2019). Managing for soil carbon sequestration: Let's get realistic. *Global Change Biology*, 25, 386–389. <https://doi.org/10.1111/gcb.14478>

- Schulz, H., & Glaser, B. (2012). Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *Journal of Plant Nutrition and Soil Science*, 175, 410–422. <https://doi.org/10.1002/jpln.201100143>
- Shinohara, Y., & Kohyama, N. (2004). Quantitative analysis of tridymite and cristobalite crystallized in rice husk ash by heating. *Industrial Health*, 42, 277–285. <https://doi.org/10.2486/indhealth.42.277>
- Silber, A., Levkovitch, I., & Graber, E. R. (2010). pH-dependent mineral release and surface properties of cornstraw biochar: Agronomic implications. *Environmental Science and Technology*, 44, 9318–9323. <https://doi.org/10.1021/es101283d>
- Smithson, F. (1956). Plant opal in soil. *Nature*, 178, 107. <https://doi.org/10.1038/178107a0>
- Sohi, S., Krull, E., Lopez-Capel, E., & Bol, R. (2010). A review of biochar and its use and function in soil. *Advances in Agronomy*, 105, 47–82. [https://doi.org/10.1016/s0065-2113\(10\)05002-9](https://doi.org/10.1016/s0065-2113(10)05002-9)
- Sombroek, W. G., Nachtergaele, F. O., & Hebel, A. (1993). Amounts, dynamics and sequestering of carbon in tropical and subtropical soils. *Ambio*, 22, 417–426.
- Sommer, M., Jochheim, H., Höhn, A., Breuer, J., Zagorski, Z., Busse, J., ... Kaczorek, D. (2013). Si cycling in a forest biogeosystem – The importance of transient state biogenic Si pools. *Biogeochemistry*, 10, 4991–5007. <https://doi.org/10.5194/bg-10-4991-2013>
- Sommer, M., Kaczorek, D., Kuz'yakov, Y., & Breuer, J. (2006). Silicon pools and fluxes in soils and landscapes—A review. *Journal of Plant Nutrition Soil Science*, 169, 310–329. <https://doi.org/10.1002/jpln.200521981>
- Song, Z., Müller, K., & Wang, H. (2014). Biogeochemical silicon cycle and carbon sequestration in agricultural ecosystems. *Earth-Science Reviews*, 139, 268–278. <https://doi.org/10.1016/j.earscirev.2014.09.009>
- Song, Z., Parr, J. F., & Guo, F. (2013). Potential of global cropland phytolith carbon sink from optimization of cropping system and fertilization. *PLoS ONE*, 8, e73747. <https://doi.org/10.1371/journal.pone.0073747>
- Song, Z., Wang, H., Strong, P. J., Li, Z., & Jiang, P. (2012). Plant impact on the coupled terrestrial biogeochemical cycles of silicon and carbon: Implications for biogeochemical carbon sequestration. *Earth-Science Reviews*, 115, 319–331. <https://doi.org/10.1016/j.earscirev.2012.09.006>
- Song, Z., Wang, H., Strong, P. J., & Shan, S. (2014). Increase of available soil silicon by Si-rich manure for sustainable rice production. *Agronomy for Sustainable Development*, 34, 813–819. <https://doi.org/10.1007/s13593-013-0202-5>
- Spokas, K., & Reicosky, D. (2009). Impacts of sixteen different biochars on soil greenhouse gas production. *Annals of Environmental Science*, 3, 179–193.
- Street-Perrott, F. A., & Barker, P. A. (2008). Biogenic silica: A neglected component of the coupled global continental biogeochemical cycles of carbon and silicon. *Earth Surface Processes Landforms*, 33, 1436–1457. <https://doi.org/10.1002/esp.1712>
- Struyf, E., & Conley, D. J. (2012). Emerging understanding of the ecosystem silica filter. *Biogeochemistry*, 107, 9–18. <https://doi.org/10.1007/s10533-011-9590-2>
- Struyf, E., Smis, A., Van Damme, S., Garnier, J., Govers, G., Van Wesemael, B., ... Meire, P. (2010). Historical land use change has lowered terrestrial silica mobilization. *Nature Communications*, 1, 129. <https://doi.org/10.1038/ncomms1128>
- Takahashi, E., Ma, J., & Miyake, Y. (1990). The possibility of silicon as an essential element for higher plants. *Comments on Agricultural Food Chemistry*, 2, 99–102. [https://doi.org/10.1016/S0928-3420\(01\)80006-9](https://doi.org/10.1016/S0928-3420(01)80006-9)
- Tan, Z., Ye, Z., Zhang, L., & Huang, Q. (2018). Application of the 15 N tracer method to study the effect of pyrolysis temperature and atmosphere on the distribution of biochar nitrogen in the biomass–biochar–plant system. *Science of the Total Environment*, 622, 79–87. <https://doi.org/10.1016/j.scitotenv.2017.11.341>
- Tréguer, P., & Pondaven, P. (2000). Global change: Silica control of carbon dioxide. *Nature*, 406, 358. <https://doi.org/10.1038/35019236>
- Trembath-Reichert, E., Wilson, J. P., Mcglyn, S. E., & Fischer, W. W. (2015). Four hundred million years of silica biomineralization in land plants. *Proceedings of the National Academy of Sciences of the United States of America*, 112, 5449–5454. <https://doi.org/10.1073/pnas.1500289112>
- Tubana, B. S., Babu, T., & Datnoff, L. E. (2016). A review of silicon in soils and plants and its role in US agriculture: History and future perspectives. *Soil Science*, 181, 393–411. <https://doi.org/10.1097/SS.0000000000000179>
- Uchimiya, M., Chang, S., & Klasson, K. T. (2011). Screening biochars for heavy metal retention in soil: Role of oxygen functional groups. *Journal of Hazardous Materials*, 190, 432–441. <https://doi.org/10.1016/j.jhazmat.2011.03.063>
- Unzué-Belmonte, D., Struyf, E., Clymans, W., Tischer, A., Potthast, K., Bremer, M., ... Schaller, J. (2016). Fire enhances solubility of biogenic silica. *Science of the Total Environment*, 572, 1289–1296. <https://doi.org/10.1016/j.scitotenv.2015.12.085>
- Uzoma, K., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A., & Nishihara, E. (2011). Effect of cow manure biochar on maize productivity under sandy soil condition. *Soil Use Management*, 27, 205–212. <https://doi.org/10.1111/j.1475-2743.2011.00340.x>
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K. Y., Downie, A., Rust, J., ... Cowie, A. (2010). Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil*, 327, 235–246. <https://doi.org/10.1007/s11104-009-0050-x>
- Vander Linden, C., & Delvaux, B. (2019). The weathering stage of tropical soils affects the soil-plant cycle of silicon, but depending on land use. *Geoderma*, 351, 209–220. <https://doi.org/10.1016/j.geoderma.2019.05.033>
- Vandevenne, F., Barão, L., Ronchi, B., Govers, G., Meire, P., Kelly, E., & Struyf, E. (2015). Silicon pools in human impacted soils of temperate zones. *Global Biogeochemical Cycles*, 29, 1439–1450. <https://doi.org/10.1002/2014GB005049>
- Vandevenne, F., Struyf, E., Clymans, W., & Meire, P. (2012). Agricultural silica harvest: Have humans created a new loop in the global silica cycle? *Frontiers in Ecology and the Environment*, 10, 243–248. <https://doi.org/10.1890/110046>
- Vanek, S. J., & Lehmann, J. (2015). Phosphorus availability to beans via interactions between mycorrhizas and biochar. *Plant and Soil*, 395, 105–123. <https://doi.org/10.1007/s11104-014-2246-y>
- Vanlauwe, B., & Giller, K. E. (2006). Popular myths around soil fertility management in sub-Saharan Africa. *Agriculture, Ecosystems & Environment*, 116, 34–46. <https://doi.org/10.1016/j.agee.2006.03.016>
- Verheijen, F., Jeffery, S., Bastos, A., & Van DerVelde, M. (2010). Biochar application to soils. In *A critical scientific review of effects on soil properties, processes and functions*. EUR 24099 EN. Luxembourg: Office for the Official Publications of the European Communities, 149 pp.

- Wang, M., Wang, J. J., & Wang, X. (2018). Effect of KOH-enhanced biochar on increasing soil plant-available silicon. *Geoderma*, 321, 22–31. <https://doi.org/10.1016/j.geoderma.2018.02.001>
- Wang, Y., Xiao, X., & Chen, B. (2018). Biochar impacts on soil silicon dissolution kinetics and their interaction mechanisms. *Scientific Reports*, 8, 8040. <https://doi.org/10.1038/s41598-018-26396-3>
- Weng, Z., Van Zwieten, L., Singh, B. P., Tavakkoli, E., Joseph, S., Macdonald, L. M., ... Cowie, A. (2017). Biochar built soil carbon over a decade by stabilizing rhizodeposits. *Nature Climate Change*, 7, 371–376. <https://doi.org/10.1038/nclimate3276>
- Wilding, L., & Drees, L. (1974). Contributions of forest opal and associated crystalline phases to fine silt and clay fractions of soils. *Clay Minerals*, 22, 295–306. <https://doi.org/10.1346/ccmn.1974.0220311>
- Wilding, L., Hallmark, C., & Smeck, N. (1979). Dissolution and stability of biogenic opal 1. *Soil Science Society of America Journal*, 43, 800–802. <https://doi.org/10.2136/sssaj1979.03615995004300040037x>
- Windeatt, J. H., Ross, A. B., Williams, P. T., Forster, P. M., Nahil, M. A., & Singh, S. (2014). Characteristics of biochars from crop residues: Potential for carbon sequestration and soil amendment. *Journal of Environmental Management*, 146, 189–197. <https://doi.org/10.1016/j.jenvman.2014.08.003>
- Woolf, D., Amonette, J. E., Street-Perrott, F. A., Lehmann, J., & Joseph, S. (2010). Sustainable biochar to mitigate global climate change. *Nature Communications*, 1, 56. <https://doi.org/10.1038/ncomms1053>
- Wu, W., Yang, M., Feng, Q., McGrouther, K., Wang, H., Lu, H., & Chen, Y. (2012). Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass and Bioenergy*, 47, 268–276. <https://doi.org/10.1016/j.biombioe.2012.09.034>
- Wu, Y., Wang, C., & Hill, D. V. (2012). The transformation of phytolith morphology as the result of their exposure to high temperature. *Microscopy Research Technique*, 75, 852–855. <https://doi.org/10.1002/jemt.22004>
- Xia, H., & Rayson, G. D. (1998). Investigation of aluminum binding to a Datura innoxia material using ^{27}Al NMR. *Environmental Science & Technology*, 32, 2688–2692. <https://doi.org/10.1021/es980171s>
- Xiao, X., Chen, B., & Zhu, L. (2014). Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures. *Environmental Science & Technology*, 48, 3411–3419. <https://doi.org/10.1021/es405676h>
- Yang, J.-L., & Zhang, G.-L. (2018). Silicon cycling by plant and its effects on soil Si translocation in a typical subtropical area. *Geoderma*, 310, 89–98. <https://doi.org/10.1016/j.geoderma.2017.08.014>
- Yang, X., Liu, J., McGrouther, K., Huang, H., Lu, K., Guo, X. I., ... Wang, H. (2016). Effect of biochar on the extractability of heavy metals (Cd, Cu, Pb, and Zn) and enzyme activity in soil. *Environmental Science and Pollution Research International*, 23, 974–984. <https://doi.org/10.1007/s11356-015-4233-0>
- Yang, X., Lu, K., McGrouther, K., Che, L., Hu, G., Wang, Q., ... Wang, H. (2017). Bioavailability of Cd and Zn in soils treated with biochars derived from tobacco stalk and dead pigs. *Journal of Soils and Sediments*, 17, 751–762. <https://doi.org/10.1007/s11368-015-1326-9>
- Yang, X., Wang, H., Strong, P., Xu, S., Liu, S., Lu, K., ... Chen, X. (2017). Thermal properties of biochars derived from waste biomass generated by agricultural and forestry sectors. *Energies*, 10, 469. <https://doi.org/10.3390/en10040469>
- Yin, J., Yang, X., & Zheng, Y. (2014). Influence of increasing combustion temperature on the AMS 14C dating of modern crop phytoliths. *Scientific Reports*, 4, 6511. <https://doi.org/10.1038/srep06511>
- Yuan, J.-H., Xu, R.-K., Qian, W., & Wang, R.-H. (2011). Comparison of the ameliorating effects on an acidic ultisol between four crop straws and their biochars. *Journal of Soils and Sediments*, 11, 741–750. <https://doi.org/10.1007/s11368-011-0365-0>
- Zama, E. F., Reid, B. J., Sun, G.-X., Yuan, H.-Y., Li, X.-M., & Zhu, Y.-G. (2018). Silicon (Si) biochar for the mitigation of arsenic (As) bioaccumulation in spinach (*Spinacia oleracea*) and improvement in the plant growth. *Journal of Cleaner Production*, 189, 386–395. <https://doi.org/10.1016/j.jclepro.2018.04.056>
- Zhang, A., Bian, R., Pan, G., Cui, L., Hussain, Q., Li, L., ... Yu, X. (2012). Effects of biochar amendment on soil quality, crop yield and greenhouse gas emission in a Chinese rice paddy: A field study of 2 consecutive rice growing cycles. *Field Crops Research*, 127, 153–160. <https://doi.org/10.1016/j.fcr.2011.11.020>
- Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., ... Huang, H. (2013). Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environmental Science Pollution Research*, 20, 8472–8483. <https://doi.org/10.1007/s11356-013-1659-0>

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Li Z, Delvaux B. Phytolith-rich biochar: A potential Si fertilizer in desilicated soils. *GCB Bioenergy*. 2019;00:1–19. <https://doi.org/10.1111/gcbb.12635>