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Effect of KOH-enhanced biochar on increasing soil plant-available silicon

Meng Wang[a,b], Jim J. Wang[b,*], Xudong Wang[a,*]

[a] College of Natural Resources and Environment, Northwest A&F University, Yangling,Shaanxi 712100, China
[b] School of Plant, Environmental and Soil Sciences, Louisiana State University Agricultural Center, Baton Rouge, LA 70803,USA

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ABSTRACT

Bio-based alternative Si fertilizers were developed by pyrolyzing Si-rich agricultural crop residue biomass of rice straw, sugarcane harvest residue, miscanthus, and switchgrass with KOH pretreatment at 0:100, 1:100, 5:100, 10:100, 25:100 and 50:100 KOH:Feedstock biomass ratios (termed 0 KB, 1 KB, 5 KB, 10 KB, 25 KB and 50 KB) and were evaluated for enhancing bioavailable Si in soils. KOH pretreatment enhanced plant-available Si in all feedstocks-derived biochars with rice straw-derived 10 KB biochar exhibiting the highest Si release. SEM-EDX mapping images showed morphological and structural changes of phytoliths in KOH-enhanced biochars which contributed to the increased bioavailable Si. Application of 1% KOH-enhanced biochars to soils significantly increased plant-available Si in soils with minimum effect on soil pH. Perennial ryegrass grown in 10 KB rice straw biochar treated soil increased Si uptake by 31% over 0 KB treated soil and was comparable with mineral Si treatment. Overall, KOH-enhanced biochar as alternative Si source could provide multiple functions in disease control, K nutrition, and C sequestration.

1. Introduction

Silicon (Si) plays a major role in plant's overall mechanic strength and defense against pathogens and insects as well as improving the intake of other nutrients, alleviating toxicity of toxic metals, and enhancing stress tolerance against drought, salts, temperature extremes (Ma and Yamaji, 2006; Epstein, 2009; Guntzer et al., 2012; Adrees et al., 2015; Keller et al., 2015). Silicon has been shown to improve rice quality and yield through a feed-forward stimulation of photosynthetic rates and alteration of primary metabolism (Detmann et al., 2012), and to enhance resistance of rice to diseases, such as brown spot (*Cochliobolus miyabeanus*) and leaf blast (*Magnaporthe*) (Datnoff et al., 2001; Savant et al., 1999). Application of Si fertilizer in Florida everglades histosols has increased sugarcane yields as much as 23% (Anderson et al., 1987). Beneficial effects following Si fertilization have been documented for many crops including rice, barley, corn, oats, soybean, sugarcane, wheats as well as pastures, vegetables and fruits such as cucumber, pepper, tomato, grapes, etc. (Snyder et al., 2007). Despite this, Si is only recently officially recognized as "plant-beneficial substance" by the Association of American Plant Food Control Officials (AAPFCO), the regulatory body that governs the labeling of fertilizers in the USA.

Silicon is the second most abundant element on earth but much of Si found in soil is not in the available form for crop uptake. On the other hand, plant Si also plays an important role in Si geochemical cycle due to the essence of its large available pool as compared to that from the weathering of silicate minerals (Derry et al., 2005). Plant Si is considered as a sustainable and renewable Si pool which can be returned to topsoil after litter fall and plant decay. However, this plant Si pool is often disrupted by crop removal for various reasons (Struyf et al., 2009; Houben et al., 2013; Vandevenne et al., 2012). Silicon is generally taken up by plant as uncharged monosilicic acid [H_4SiO_4] and irreversibly deposited as polymerized silica gel (SiO_2-nH_2O), known as phytoliths (Raven, 1983; Epstein, 2009). The amount of phytoliths is proportional to the silicon concentration in a plant, and approximately 90% silicon accumulated inside plant is in phytolith form (Song et al., 2014). The phytoliths are highly soluble, and the solubility is close to that of amorphous silica and is 17 times higher than quartz (Fraysse et al., 2006, 2009).

The most common silicon fertilizers are wollastonite and slag. Wollastonite is considered to be the most efficient silicon fertilizer for soil application due to that it can release the largest amount of plant-available silicon (2.31–3.6%) into soil solution for plant uptake (Sebastian et al., 2013; Buck et al., 2010). However, its use is often limited because of its relatively high cost. On the other hand, silica slags from industrial waste materials such as blast-furnace and silicon-manganese slag of steel manufacturing, and electric furnace slag of phosphorus production are used as a low-cost Si fertilizer (Savant et al., 1999). The issue with these slag materials is that they often contain a variety of heavy metals which could cause biotic damage to plant and

* Corresponding authors.
E-mail addresses: jjwang@agcenter.lsu.edu (J.J. Wang), wangxd@nwsuaf.edu.cn (X. Wang).

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Table 1
Chemical and physical properties of feedstocks and KOH-enhanced biochars from rice straw, miscanthus, sugarcane harvest residue, and switchgrass[a].

Materials	Yield	pH	Ash	C	H	N	P	K	Ca	Mg	Al	Fe
	%		%	%	%	%	$g\,kg^{-1}$	$g\,kg^{-1}$	$g\,kg^{-1}$	$g\,kg^{-1}$	$g\,kg^{-1}$	$g\,kg^{-1}$
Rice straw												
FS	–	6.19	17.00	38.82	4.04	1.12	0.90	11.72	1.90	1.75	0.28	0.16
0 KB	35.34	9.59	45.12	45.03	1.269	2.19	1.84	16.09	4.45	3.15	0.45	0.30
1 KB	36.71	9.86	48.48	43.44	1.145	1.71	1.87	26.54	4.72	3.23	0.48	0.32
5 KB	37.14	10.22	52.69	41.26	0.94	1.23	1.80	86.02	4.47	3.09	0.51	0.32
10 KB	39.00	10.51	57.93	34.21	0.75	1.00	1.75	138.46	4.39	3.09	0.46	0.31
25 KB	44.35	10.78	69.33	26.80	0.528	0.68	1.38	254.98	3.56	2.39	0.30	0.24
50 KB	53.21	10.86	82.05	20.15	0.358	0.62	1.10	378.33	2.86	1.91	0.24	0.20
Miscanthus												
FS	–	5.87	6.52	47.83	5.42	0.56	1.63	6.89	3.53	0.94	0.03	0.08
0 KB	30.26	9.56	20.57	67.08	1.86	1.25	5.05	17.96	11.82	2.71	0.10	0.25
1 KB	28.14	9.66	24.41	65.44	1.77	1.19	5.50	33.70	13.01	3.00	0.14	0.29
5 KB	30.44	10.07	34.52	63.14	1.81	0.95	4.75	96.37	11.10	2.58	0.12	0.25
10 KB	31.67	10.43	48.10	56.34	1.82	0.83	4.18	158.31	9.94	2.23	0.11	0.21
25 KB	38.78	10.56	65.70	44.33	1.94	0.55	3.07	300.47	7.49	1.68	0.08	0.16
50 KB	47.32	10.84	81.75	25.78	1.4	0.19	1.95	376.14	4.79	1.12	0.05	0.11
Sugarcane harvest residue												
FS	–	6.38	6.95	45.62	5.32	1.31	1.48	11.56	4.16	1.70	0.02	0.06
0 KB	30.90	9.63	21.05	68.58	1.851	1.67	5.01	35.75	14.00	5.40	0.06	0.23
1 KB	28.10	9.75	25.91	65.86	1.717	1.48	5.44	55.31	15.28	5.83	0.08	0.25
5 KB	30.36	10.03	43.62	60.87	1.752	1.36	4.31	79.77	12.48	4.67	0.07	0.22
10 KB	31.29	10.35	50.74	58.72	1.642	1.11	3.84	183.78	10.97	4.10	0.07	0.19
25 KB	38.94	10.60	69.48	38.89	1.462	0.69	2.58	274.92	8.11	3.02	0.05	0.14
50 KB	47.84	10.84	83.54	27.94	1.58	0.3	1.76	366.11	5.38	2.03	0.04	0.10
Switchgrass												
FS	–	4.48	2.07	45.20	5.35	0.89	0.66	4.57	1.86	1.29	0.04	0.05
0 KB	29.08	9.52	9.48	80.75	2.14	0.65	2.02	13.31	7.00	4.33	0.15	0.19
1 KB	27.86	9.61	15.00	79.55	1.88	0.67	1.98	24.99	7.17	4.21	0.72	0.21
5 KB	29.58	9.94	28.95	71.32	1.9	0.53	1.65	126.41	5.67	3.40	0.43	0.16
10 KB	31.58	10.32	39.66	64.17	1.59	0.42	1.54	180.73	5.10	3.04	0.62	0.15
25 KB	37.41	10.64	62.66	47.22	1.77	0.35	1.30	322.29	4.24	2.54	0.30	0.13
50 KB	48.37	11.02	78.10	33.29	1.53	0.27	0.76	354.74	2.47	1.44	0.26	0.10

Biochar pH was measured based on 1:100 solid to solution ratio. Total P, K, Ca, Mg, Al and Fe were determined by digestion using nitric acid and H_2O_2 followed by ICP-OES analysis except for C, N, and H, which were determined by dry combustion. FS, feedstock; 0 KB, 1 KB…50 KB indicate the biochars prepared at the proportion of KOH to feedstock of 0, 1…50.
[a] All values are averages of two replicates.

pollution in the environment. For instance, some steel slags were found to have as much as 1.1% of Cr along with Fe (43%), Mg (26%), and Mn (4.6%) (Garcia-Guinea et al., 2010). Leaching test of electric arc furnace slag and ladle slag also showed an increase of heavy metal releases with ageing (Gomes, 2006). Therefore, an alternative and inexpensive Si source is urgently needed.

Recently, much attention has been paid to biochar as soil amendment. Biochar, produced from the conversion of biomass under oxygen depletion condition, has been shown to enhance soil quality, fertility, carbon sequestration and alleviate trace elements toxicity in plants (Lehmann and Joseph, 2009; Powlson et al., 2011; Rizwan et al., 2016). On the other hand, biochar amendment was also shown to improve soil plant-available Si content and shoot Si uptake by various crops (Liu et al., 2014; Abbas et al., 2017). Research on Si dissolution kinetics of different temperature-pyrolyzed biochars found that biochar produced at 500 °C could release as much as 43 $mg\,kg^{-1}$ slow-releasable bioavailable Si (Xiao et al., 2014). Moreover, the Si released from biochar could be absorbed by the plants and coordinated with Al to form Al-Si compounds in the epidermis of wheat roots to alleviate Al toxicity (Qian et al., 2016). In addition, Si could alleviate Cu toxicity symptoms by selectilvely increasing the absorption of other essential elements (Keller et al., 2015). These results suggest that plant residue biomass, especially those of high-Si accumulating, could be used for producing potentially biochar-based bioavailable Si for crop production. In addition, the relation between Si and carbon in plant and soil has been noted (Harrison, 1996; Parr et al., 2010). Various studies have showed that phytoliths occlude 1–6% of organic C (phytolith-occluded carbon, PhytOC) (Harrison, 1996; Parr et al., 2010), which is highly resistant against degradation than other soil organic carbon (SOC) fraction because of the protection of silica (Meunier et al., 1999; Parr and Sullivan, 2005). Phytoliths are estimated to contribute 15–37% of the stable soil C sink (Parr and Sullivan, 2005). Since phytoliths are stable up to 500–800 °C, pyrolyzed biomass at these temperatures should still contain primarily unmodified silicon (Krull et al., 2003). Although Si plays a pivotal role in carbon sequestration, the interaction between Si availability and C stability following biochar soil application has not been fully evaluated.

Agricultural wastes such as rice and sugarcane harvest crop residues contain considerable amounts of Si (Savant et al., 1999; Currie and Perry, 2007). Biofuel plants such as miscanthus and switchgrass also contain 1.7–2.0% Si (Nabity et al., 2012). In addition, recent research on carbonation of biomass showed that higher Si-accumulating plants do not necessarily release higher bioavailable Si by thermal treatment (Houben et al., 2013). On the other hand, it is known that pH and dissolution rate of Si or phytoliths is positively correlated (Fraysse et al., 2006). This suggests that through alkaline pretreatment of crop biomass, it is possible to enhance the solubility of Si or phytoliths. Therefore, in this study, four Si-accumulating crop residues were used as feedstocks, pretreated with various rates of alkaline materials, and optimized for development of biochar-based Si source as alternative fertilizer. The Si release characteristics of these converted materials were evaluated.