pH-Dependent Mineral Release and Surface Properties of Cornstraw Biochar: Agronomic Implications

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SUPPORTING INFORMATION

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Determination of pH-dependent CEC and AEC. Determination (in duplicate) of CEC and AEC of the CS_{Ac} biochar included three steps: (i) 1 g biochar (W_{BC}) was placed in a pre-weighed 50 ml centrifuge tube with 40 mL of 1M NaCI solution and shaken for 1 h. After centrifugation (25,314g), the supernatant was decanted and the biochar treated three more times with 1M NaC1. The suspensions were adjusted overnight to the desired pH with 0.1M HC1 or NaOH. (ii) Excess soluble salts were washed from the samples with NaCl solutions of decreasing ionic strength to 0.05 M, with pH adjustment when necessary. The pH value of the final solution was determined as that of the corresponding CEC and AEC, and solutions were retained for Na and Cl analyses. Tubes with entrained NaC1 solution were weighed, and the amount of entrained Na and Cl (Q_{Na} and Q_{Cl}, respectively) was calculated by multiplying the Na and Cl concentration by the volume of the entrained NaC1 solution. (iii) Adsorbed NaC1 was displaced with 1M KNO_3 solution adjusted to the desired pH with 0.1N HNO_3 or KOH. The suspensions were shaken for 1 h and the supernatant was collected after centrifugation. This step was repeated in triplicate, following which the Na and Cl concentrations (C_{Na} and C_{Cl}, respectively) and the volume of the displacement solution (V_{KNO3}) were determined. CEC and AEC were calculated as follows:

$$CEC = [(C_{Na}) (V_{KNO3}) - (Q_{Na})] / (W_{BC})$$

$$AEC = [(C_{Cl}) (V_{KNO3}) - (Q_{Cl})] / (W_{BC})$$

Kinetics of pH-dependent element release from cornstraw biochar. Kinetics of element release from CS biochar was tested at four solution-pH values in duplicate. CS biochar (0.5 grams) was added to a 50 ml centrifuge tube containing 25 ml of 0.01 M NaCl solution. Following an overnight pre-equilibrium period, pH was adjusted to the predetermined values by adding 0.1 M HCl. The tubes were shaken and kept in darkness at 30°C and equilibration continued for 1, 3.5,

7, 24, 50, 73, 144, 168, 336 and 505 h. pH was adjusted throughout the experiment by adding appropriate amounts of 0.1 M HCI as needed. At the end of each time step, pH and electrical conductivity (EC) were determined, aliquots were filtered through a 0.45-μm membrane (Millipore Corporation, Bedford, Ma), and the supernatants were acidified to pH 2 and stored pending chemical analysis. Element concentrations were determined as follows: P with an injector Lachat Autoanalyzer (Lachat Instruments, Milwaukee, WI, USA); Na and K with a flame photometer (M410, Sherwood Sci. Ltd, Cambridge, England); Ca, Mg, Fe, Zn and Mn with an Analyst 800 atomic absorption spectrophotometer (Perkin Elmer, Shelton, CT, USA).

Potentiometric titrations and effects of ionic strength and pH on element solubilization. One g each of both biochar samples (water and acid-washed, CS and CS_{Ac}, respectively) was added to 100-ml Erlenmeyer flasks containing with 50 mL of 0.001, 0.01 and 0.1 M NaCl solutions, in duplicate. The suspensions were maintained overnight for a pre-equilibrium period, following which pH was adjusted to the predetermined values by adding 0.1 M HC1 or NaOH. The Erlenmeyer flasks were shaken for 48 h while keeping pH constant by adding HC1 or NaOH as necessary. Supernatants were handled and element concentrations determined as above.

Determination of pH-dependent surface properties. Kinetics of element release from CS biochar into 0.01 M NaCl solution over a total of 505 h was also tested at four solution pH values. Potentiometric titrations and the effect of ionic strength and pH on element solubilization was tested at 48 hr at three ionic strengths (0.001, 0.01 and 0.1 M NaCl) and 6 pH levels, and element concentrations were determined as follows: P with an injector Lachat Autoanalyzer (Lachat Instruments); Na and K with a flame photometer (M410, Sherwood Sci. Ltd); Ca, Mg, Fe, Zn and Mn with an Analyst 800 atomic absorption spectrophotometer (Perkin Elmer).

Table S-1. Chemical analyses of the biochars. P, K, Ca, Mg, Na, Fe, Zn, Mn, and Al were determined for the cornstraw biochar (CS) by digestion in 70% HNO_3 for 24h at 120ºC. Element concentrations in the HNO_3 solutions were determined by inductively coupled plasma (ICP-AES Arcos, EOP model, Spectro Ltd). Standard errors are given in parenthesis. Ash content (in triplicate) of both CS and CS_{AC} biochars was determined by weight loss after heating to 550ºC in an oxygen atmosphere for 4 h. Total C, H, N, O, and S of both CS and CS_{AC} biochars were determined in triplicate by element analyzer (Thermo Flash EA-1112 Elemental Analyzer). Results for acidified biochar (CS_{AC}) are noted in square brackets.

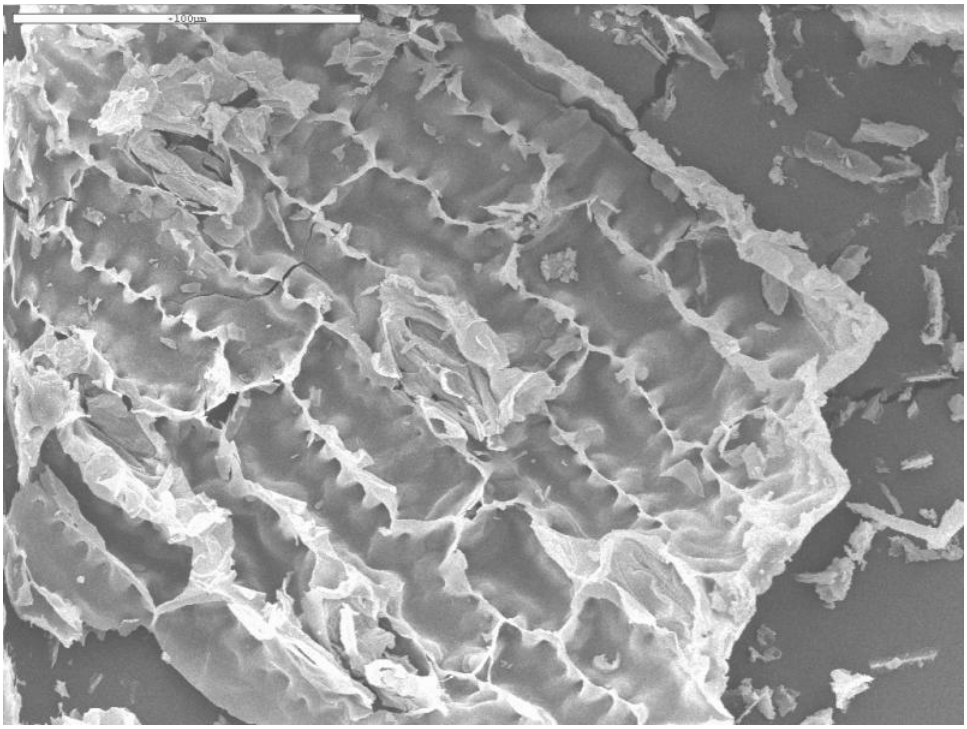
Element	**Content**
P (mg kg^{-1})	3,770 (5)
K (mg kg^{-1})	48,700 (586)
Ca (mg kg^{-1})	19,800 (73)
Mg (mg kg^{-1})	7,655 (40)
Na (mg kg^{-1})	2,590 (28)
Fe (mg kg^{-1})	1,990 (10)
Zn (mg kg^{-1})	85 (2)
Mn (mg kg^{-1})	139 (2)
Al (mg kg^{-1})	1,480 (13)
Ash (%)	32.5±0.4 [20.1±0.1]
N (%)	1.4±0.2 [2.7±0.9]
C (%)	50.2±2.2 [61.6±1.8]
S (%)	0.2±0.3 [0.00±0.00]

H (%)	1.9±0.3 [2.2±0.2]
O (%) (by difference)	13.6±2.3 [13.5±2.0]
O/C	0.21±0.04 [0.16±0.02]
H/C	0.46±0.08 [0.42±0.03]
C/N	40.93±5.72 [26.90±9.50]
H/O	2.25±0.55 [2.59±0.42]

Table S-2. Best fitted R_P, R_{Ca}, and R_{Mg} values (SE in brackets), calculated by with Eq. [1] using data presented in Fig. 3a, c and d, respectively.

Parameter	**pH**	**Fitted value**	r^2
R_P	4.5	0.022(0.0056)	0.75
	5.7	0.021(0.0031	0.90
	6.9	0.016(0.0025)	0.81
	8.9	0.015(0.0030)	0.84
R_{Ca}	4.5	0.111(0.0185)	0.90
	5.7	0.091(0.0129)	0.66
	6.9	0.049(0.0101)	0.55
	8.9	0.020(0.0017)	0.97
R_{Mg}	4.5	0.164(0.0146)	0.98
	5.7	0.129(0.0210)	0.99
	6.9	0.108(0.089)	0.86
	8.9	0.055(0.0051)	0.96

Figure S-1. Photomicrographs from scanning electron microscopy (SEM) of intact and acidified cornstraw biochars (top and bottom, respectively). Scale bar in top photo is 100 microns; scale bar in bottom photo is 50 microns.



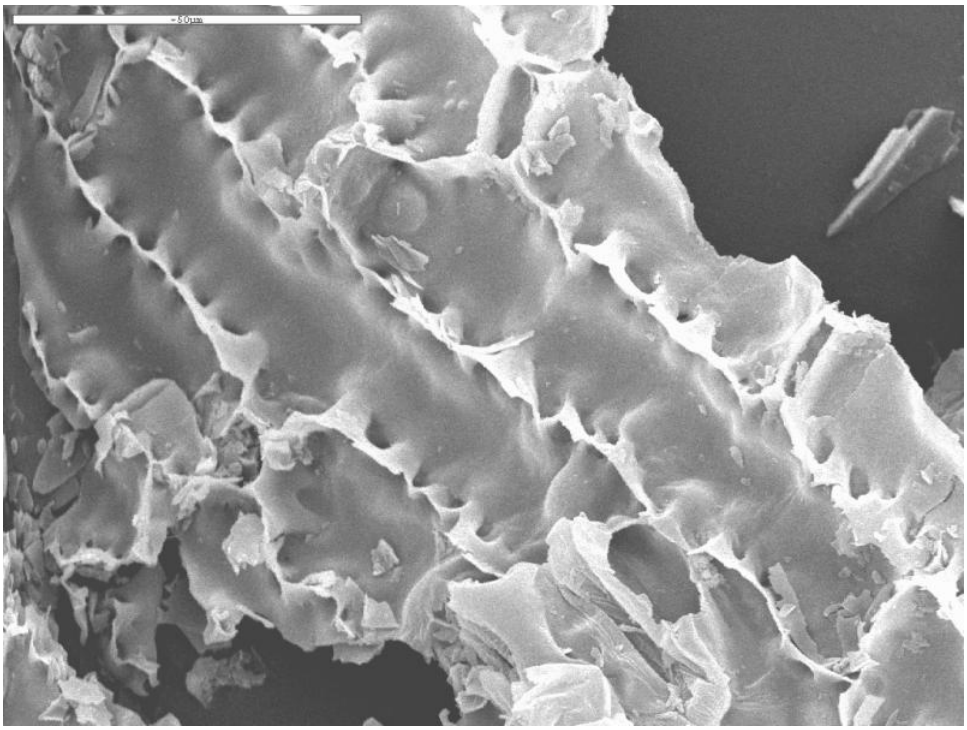


Figure S-2. XRD diffraction for the CS biochar, numbers indicates peaks (nm). The X-ray diffraction analysis was carried out on a Philips XRD diffractometer PW1830/3710/3020 with the following parameters: CuKα radiation, 40 KV tension, 30 mA current, divergence slit - 1º, receiving slit - 0.1 mm and scatter slit - of 1º, and a monochromator. Running rate: 1º 2θ/1min. The APD software controlled the diffractometer run, calculated and printed peak locations and relative intensities, and controlled the diffractogram printout. Bulk ground samples were side loaded.

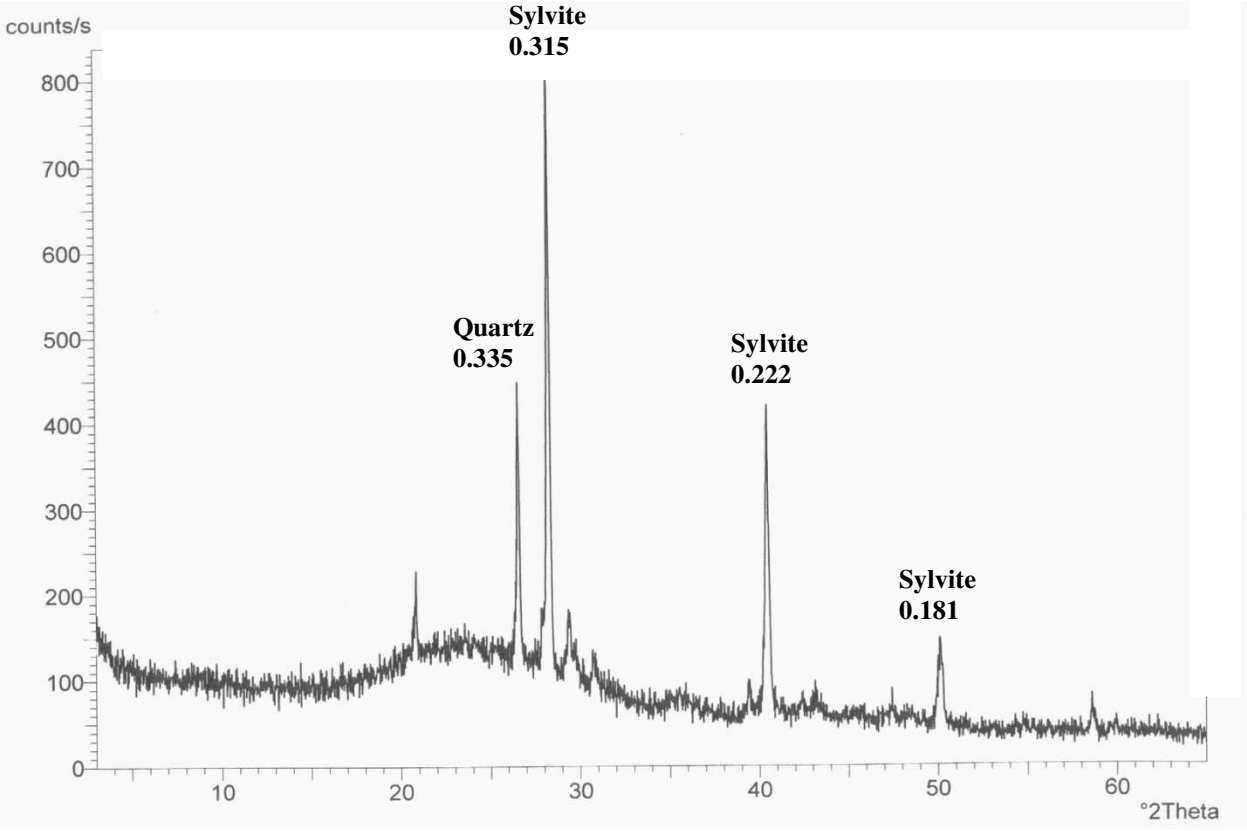


Figure S-3. FTIR spectra of CS and CS_{AC} biochars. FTIR absorbance spectra of KBr pellets prepared with 0.6% wt biochar were recorded between 400 and 4000 cm^{-1} with one hundred scans averaged with a resolution of 4 cm^{-1} (Bruker Tensor 27 FTIR Spectrometer). Only small differences are observed. In the acidified biochar (CS_{AC}), there is a small increase in the aromatic carbonyl/carboxyl C=O stretching band at 1700 cm^{-1}, and a decrease in the aromatic C=C ring stretching band at about 1400 cm^{-1} as compared with the original biochar (CS; assignments after (*1*)). The band at 1600 cm^{-1} is assigned to aromatic C=C stretching. The broad band at 1300–1000 cm^{-1} (with peak at 1080 cm^{-1}) is assigned to asymmetric stretching mode of the Si–O–Si moiety, and the two small bands at about 800 and 450 cm^{-1} are assigned to symmetric stretching and rocking modes of the Si–O–Si vibrations (*2*).Silica makes up a major part of the mineral portion of cornstraw and cornstraw biochar (*3*). The prominent band in both samples with peak absorbance at 3400 cm-1 represents –OH stretching.

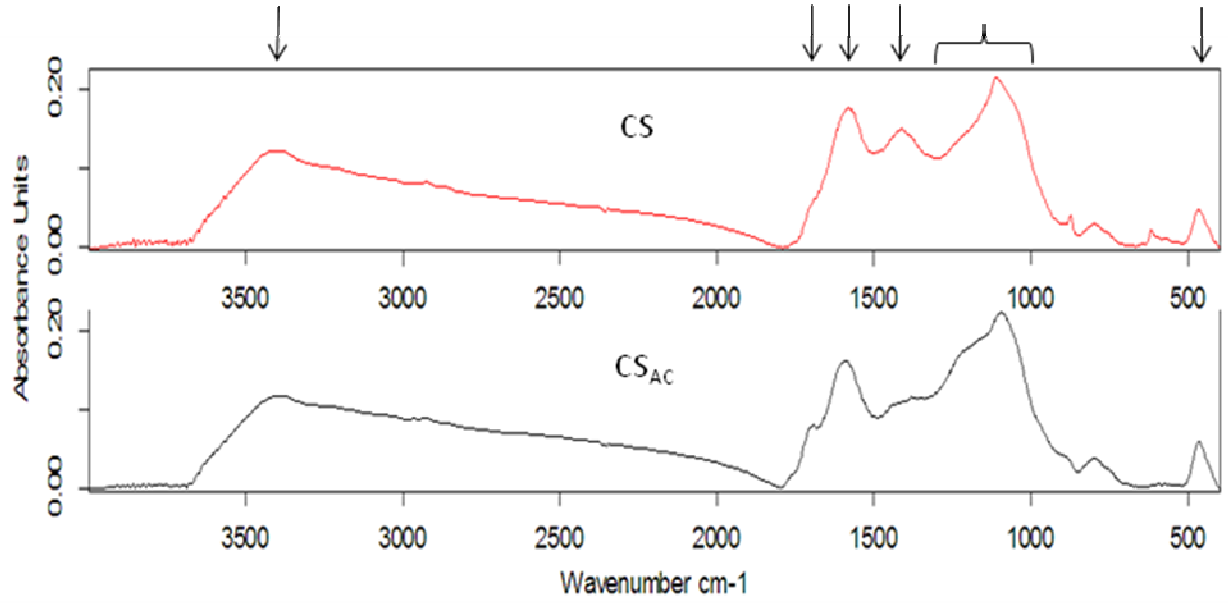


Figure S-4. The effects of pH and ionic strength (0.001, 0.01 and 0.1 M NaCl) on solution-P concentrations in intact cornstraw biochar. Biochar:solution ratio of 1:50; equilibrium period of 48 h. Symbols represent experimental data ± SE (SE not shown when smaller than the symbol) and the lines connect experimental data.