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The Potential Benefits and Limitations of Corn Cob and Sewage Sludge Biochars in an Infertile Oxisol

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Abstract: The thermal conversion of sewage sludge to biochar offers a promising alternative use for a hazardous waste material with potential benefits to agricultural productivity and soil quality. Three short-term greenhouse experiments were conducted to evaluate the effect of corn cob (CC) and sewage sludge (SS) biochars, with their anaerobically treated counterparts, on soil properties and plant growth in an infertile Oxisol. The anaerobically treated SS biochar showed the greatest concentration of bioavailable essential nutrients, but treatment only resulted in increased yields for the SS biochar in the first crop in the absence of added fertilizer. Both CC and SS biochars in combination with fertilizer doubled plant growth compared to the control in the first crop cycle, produced no significant effect in the second cycle, and more than tripled plant growth for the SS biochars in the third cycle. High ash content with high nutrient contributions (especially P) and a persistent liming effect explain the benefits of the SS biochars to plant growth. The SS biochar showed promise in mitigating the negative effects of soil Mn toxicity. Sewage sludge biochars reduced Cd bioavailability and had no significant effect on the bioavailability of other potentially toxic metals compared to the control.

Keywords: biochar; sewage sludge; soil fertility; ash content; liming effect; plant growth

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1. Introduction

Managing sewage sludge is one of the most challenging and urgent problems facing an increasingly urban global population [1]. A growing urban global population has resulted in alarming increases in sludge production; China, for example, produced approximately 5 M T of dewatered sludge in 2009 up from 3.5 M T in 1998 [2] whereas recent estimates show that the European Union produces more than 10 M T annually [3], and in the United States according to the latest available data annual sludge production is approximately 6.5 MT [4]. Traditional methods of disposal (land application, incineration, and landfilling) pose significant threats to environmental quality and human health [1]. In island environments where land is limited, sludge disposal is of particular concern. In Hawaii, for instance, rapid population growth and urbanization on the island of Oahu and limited landfill capacity has forced the consideration of alternatives to sludge disposal in landfills [5].

Thermal conversion of waste biomass to biochar offers a range of proposed benefits to agriculture and society as a whole [6–9]. Of particular interest, is the opportunity to convert hazardous materials such as sewage sludge into biochar, which when added to soils has the potential to improve soil quality and crop performance [10–12]. Sewage sludge derived biochars are typically high in mineral ash content, which could serve as a source of soluble essential plant nutrients and contribute liming potential in acidic soils [13]. While there is an interest in the use of sewage sludge biochars to increase soil productivity and an increasing number of studies characterizing the properties of sewage sludge derived biochars [14–18], there are limited studies showing benefits of sewage sludge biochar to plant growth [19–22]. There is a large and growing body of literature indicating that biochar applications to soil increase crop productivity and improve soil fertility and quality [23]. From an agronomic perspective, some of the benefits of biochar to soils include increased soil porosity and water holding capacity, increased aeration, increased aggregate stability, reductions in bulk density and tensile strength [24], augmented nutrient retention through enhanced cation exchange capacity [25], direct contribution of essential plant nutrients [26,27], a liming effect mitigating of nutrient deficiencies and elemental toxicities in acid soils [13,28], enhancement of plant-microbe symbioses [29], and more recently observations indicating possible stimulatory effects on plant phytohormones [30]. Along with the apparent benefits, there are reported negative effects from the application of some biochars to soil [7,23]; specifically, reduced soil N resulting in stunted plant growth [28,31] potential phytoxic effects from biochar derived polycyclic aromatic hyrocarbons (PAHs) [32,33], and some evidence for increased bioavailability of As [34].

Biochar's absorbant properties lend its use as an effective material in remediating contaminated soils [35–37], reducing bioavailability of heavy metals [21,38] in soils and water [39,40], and as a substrate supporting enhanced microbial colonization in anaerobic digestion systems [41]. In addition to its ability to promote microbe colonization and increase the efficiency of anaerobic digestion systems, biochar has the capacity to adsorb essential plant nutrients such as inorganic N and P [42,43] during the digestion process imparting a potential fertilizer value to the biochar. Two recent studies suggest that biochar surfaces sorbed a high amount of inorganic P under controlled conditions, and that the P was bioavailable when the biochar was added to soil stimulating plant growth [44,45].

Given the critical need to find alternative strategies for improving waste water management and sewage sludge disposal, the overall goal of this study was to evaluate the use of sewage sludge biochar to improve crop growth in an infertile soil. Specific objectives were (1) to compare the effect of a high ash sewage sludge biochar with a lower ash corn cob biochar on corn growth; and (2) to evaluate whether using both biochars in an anaerobic digestion system improved their fertilizer value when applied to soil. We hypothesized that the high ash sewage sludge biochar would increase crop growth more than the corn cob biochar, and that both anaerobically treated biochars would be enriched in N and P and increase crop growth above their untreated counterparts.

2. Materials and Methods

2.1. Biochars

Corn cob feedstock was obtained from waste piles at the Pioneer Seed Company facility located in Central Oahu in 2011. Sewage sludge was obtained from the Hawaii Kai wastewater treatment plant, Honolulu County, in 2011 (a secondary treatment facility). Both feedstocks were carbonized utilizing the Flash Carbonization process where the de-watered feedstocks were placed in a pressurized canister (1.14 MPa) and carbonized with maximum temperature reaching 600 °C for 20 min [46]. Following carbonization of each feedstock, the biochars were homogenized, and separated into two batches. One batch of each biochar was sent for use as a biofilm support material in a high rate anaerobic digestion apparatus used to remediate wastewater separated from grease trap waste [41]. The remaining batches were stored at room temperature in ziplock bags. Following their use in the anaerobic digestion experiments, the CC and SS biochars were removed from the digestors and air-dried in the laboratory. The treated and untreated biochars were crushed to pass a 2 mm sieve, and a subsample of each collected for analysis.

The uncarbonized feedstock and the treated and untreated biochars were sent to Hazen Laboratories (Hazen Research, Inc., Golden, CO, USA) where they were analyzed for proximate and ultimate analysis, main ash elements according to ASTM D2795 and ASTM D3682, respectively, and heavy metals according to Environmental Protection Agency EPA series 7000 methods. Total C (TC) and total N (TN) content of the biochars were determined by dry combustion on a LECO CN-2000 (St. Joseph, MI, USA). Biochar pH was measured in 1:1 slurry of biochar to deionized water.

Extractable base cations (Ca^{2+}, K^+, Mg^{2+}, Na^+) and cation exchange capacity [47] were measured in a 1 *M* ammonium acetate solution buffered at pH 7, P was analyzed colorimetrically by the Murphy and Riley method in a 0.5 *M* $NaHCO_3$ extract (Olsens) [48], and exchangeable NH_4^+ and NO_3^--N in a 2 *M* KCl extract. Cations were measured by inductive coupled plasma mass spectrometry on a Thermo Jarrell Ash Atom Scan 16 instrument (Franklin, MA, USA), and NH_4^+ and NO_3-N were determined by the salicylate-hypochlorite method [49] and NO_3^- by cadmium reduction [50], respectively, using an EasyChem discrete analyzer (Oak Brook, IL, UAS).

2.2. Greenhouse Experiments

A series of greenhouse biossays were installed to investigate the effect of biochar applications on soil properties and corn growth in an infertile Oxisol (Wahiawa series, very fine, kaolinitic, isohyperthermic, Rhodic Haplustox). The soil is a silty clay with pH of 6.15, total organic carbon (TOC) and TN of 12.6 and 1.50 $g \cdot kg^{-1}$, respectively, and extractable P, K, Ca, Mg and Na of 8.31, 427, 686, 219, and 54.6 $mg \cdot kg^{-1}$, respectively. Treatments consisted of four biochars, untreated corncob (CC UT) and sewage sludge (SS UT) and their treated counterparts (CC T and SS T) applied to the soil at a 2.5% (w/w) loading rate each with and without a complete fertilizer application. There were two control treatments—the unamended soil and the soil with the complete fertilizer. All treatments were replicated four times.

The experiments were conducted in sequence between August 2011 and March 2012 beginning with the sewage sludge biochars. Biochar treatments were mixed thoroughly with 2.1 kg of oven dry equivalent soil and the soil mixtures were packed into plastic pots (diam. = 0.16 m, vol. = 3016 cm^3) to achieve a bulk density of approximately 1.1 $Mg \cdot m^{-3}$, brought to 50% moisture content (w/w), which is equivalent to approximately -33 kPa [51], and allowed to stabilize in the greenhouse for two weeks replenishing water twice weekly. Eight seeds of maize (*Zea mays*, L cv. Super Sweet #9) were planted and thinned to 2 plants per pot ten days after planting. A complete fertilizer containing 100 mg N and K per kg soil as NH_4NO_3 and KCl, 100 mg P as $Ca(H_2PO_4)_2$ (this high rate was required to account for the high P fixation capacity of the Wahiawa soil); magnesium at 100 $mg \cdot kg^{-1}$ as $MgCl_2 \cdot 6H_2O$; and zinc (Zn) at 10 $mg \cdot kg^{-1}$ as $ZnSO_4 \cdot 7H_2O$ was applied in solution at planting. Two weeks after planting, an additional 50 mg N and K per kg soil were applied in solution. Soil water was maintained at 50% (w/w) and was corrected every 2–3 days by weighing the pots and adding water to return pots to original water content (during watering events careful attention was taken to minimize water loss due to leaching). The above ground biomass was harvested after five weeks, dried at 70 °C for 72 h, and weighed for dry biomass. Roots were separated from the soil by hand, washed carefully, dried, and weighed. Soils were mixed thoroughly, a 100 g sub-sample removed for analysis, stored at 4 °C prior to laboratory analyses, and the remaining soil returned to their respective pots for follow-up experiments. The same procedure was employed for the 2nd and 3rd crops, except that fertilizer applications included N, K and Zn at the rates mentioned above, but P and Mg applications were reduced to 40 $mg \cdot kg^{-1}$.

2.3. Soil and Plant Analyses

At the end of each corn growth cycle, dried above ground biomass was ground in a Wiley mill, sieved to pass 20-mesh, and total elemental concentrations (N, P, K, Ca, Mg, B, Mn, Zn, Cu, Fe, As, Cd, Co, Cr, Ni, Pb, and Se) were determined on a 0.50-g dried tissue samples digested in HNO_3/H_2O_2 (1/1 v/v) [52]. Soil pH, TOC, TN, P and extractable base cations were analyzed according to the procedures outlined for biochar analysis. The soils from the third crop cycle were extracted for Mn in a saturated paste and analyzed by ICP [53]. Due to the lack of sufficient soil samples, replicates 1 and 2, and 3 and 4 were pooled, homogenized, and analyzed separately for a total of 6 samples.

2.4. Statistical Analyses

Statistical analysis was performed separately on each crop cycle for the two biochars because the experiments were not run concurrently. Treatment effects on plant growth and soil properties were analyzed by one-way ANOVA using PROC ANOVA in SAS 9.2 (SAS Institute, Inc., Middleton, MA, USA, 2002). Where data did not mean the assumption of equal variances, ANOVA was performed on transformed data, but reported in their untransformed format. In case of significant effects, multiple mean comparisons were done using Tukey's Studentized post-hoc procedures at $P < 0.05$.

3. Results

3.1. Biochars

As expected, the CC and SS biochars showed contrasting chemical properties and variable response to carbonization (Table 1). The CC biochar was C-rich, but low in N, S and ash constituents compared with the sludge biochar. Low O:C and H:C ratios and low VM content in both of the untreated biochars indicate a high level of thermal alteration and aromaticity. Especially noteworthy were the very high ash and N contents in the SS biochar. The main ash components of the two biochars were considerably different and responded differently to carbonization. The CC biochar showed depletions in SiO_2 and CaO and enrichments in MgO, Na_2O, K_2O, and P_2O_5 compared to the feedstock whereas carbonization had minimal effects on ash constituents in the SS material. Thermal treatment tended to concentrate heavy metals in both biochars with increases more substantial for the sewage sludge materials.

Table 1. Ultimate, proximate, ash components and heavy metal analyses for untreated (UT) and treated (T) † corn cob (CC) and Hawaii Kai sewage sludge (SS) biochars and feedstocks.

Biochar	Ultimate Analysis					Proximate Analysis				
	C	H	O	N	S	FC [a]	VM [b]	ash		
				%						
CC [c]	48.7	5.75	42.2	0.51	0.06	NA	NA	2.83		
CC UT	84.9	2.42	2.66	0.89	0.13	80.3	8.26	11.4		
CC T	84.3	2.80	4.47	0.91	0.16	84.8	9.64	5.61		
SS [c]	37.7	5.22	14.6	7.05	3.58	NA	NA	31.9		
SS UT	30.2	1.29	<0.01	3.13	3.81	25.8	8.64	65.5		
SS T	30.5	0.54	<0.01	2.62	4.26	25.2	4.29	70.5		
	Main Ash Components									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3
					%					
CC [c]	52.1	1.52	1.30	0.13	2.46	1.90	0.36	21.00	8.56	2.54
CC UT	22.2	1.57	5.41	0.25	1.79	2.64	7.19	36.9	10.1	2.84
CC T	20.1	1.45	4.54	0.24	1.62	3.31	11.0	23.6	12.7	4.03
SS [c]	13.4	4.79	23.3	1.17	9.11	3.69	8.44	2.36	21.3	12.5
SS UT	14.4	5.68	21.2	1.39	9.13	3.99	8.61	2.13	20.9	11.9
SS T	14.5	5.79	22.5	1.46	9.41	4.29	5.42	1.91	22.4	10.6
	Heavy Metals									
	As	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn
					$mg \cdot kg^{-1}$					
CC [c]	0.18	0.1	9.56	4.27	<0.01	2.8	1	1.5	<0.05	35.1
CC UT	0.56	0.5	24.7	24	0.59	16.4	14	2.1	0.89	164
SS [c]	4.66	3.2	65	346	0.28	9	27	14	8.58	1030
SS UT	16.7	6.0	170	712	0.11	13	71	60	14.0	2360
SS T	18.2	7.0	182	766	<0.01	24	74	81	14.9	3190
USEPA [d]	75	85	NR	4300	57	75	420	840	100	7500
Hawaii [e]	20	15	200	1500	10	15	100	300	25	2000

[a] fixed carbon; [b] volatile matter; [c] raw material, [d] ceiling concentrations US EPA [54], [e] ceiling concentrations for State of Hawaii [55]; † insufficient sample for analysis.

The biochar materials showed inconsistent response to anaerobic treatment. Ash content was reduced 2-fold in the treated CC biochar, but showed an increase for the treated SS biochar. For N and S, the CC biochar showed only small changes while treatment reduced N and increased S concentrations. Treatment effects were more consistent with regards to the ash constituents where treatment increased MgO, Na_2O, and P_2O_5, but reduced K_2O compared with the untreated biochars. The pronounced loss of K_2O in the treated CC biochar was the most noteworthy effect of treatment on the ash constituents. For the SS biochars, treatment, generally, showed an increase in all metals except Hg.

The biochars showed large differences in pH and the readily soluble fraction of macronutrients and Na (Table 2). The CC biochars were alkaline whereas the SS biochars were slightly acidic. The untreated SS biochar showed higher concentrations of soluble NH_4^+-N, P, Ca and Na, but lower K and Mg compared to the CC biochar. For both treated biochars, treatment increased P, Ca and Mg with the increases more pronounced in the SS biochar. There was a consistent loss of K in both treated biochars compared to their untreated counterparts, but for NH_4^+-N and Na treatment had opposite effects on the two biochars; for the CC biochar treatment increased both NH_4^+-N and Na while treatment showed considerable reductions in the concentrations of these two elements in the SS biochar.

Table 2. Biochar pH, CEC, and concentrations of extractable nutrients. Values represent the mean of three replicates, values in parentheses are one standard deviation.

Sample	pH	CEC	NH_4^+-N	NO_3^--N	P	K^+	Ca^{++}	Mg^{++}	Na^+
		$cmol_c \cdot kg^{-1}$				$mg \cdot kg^{-1}$			
CC UT	9.20(0.03)	11.3(1.27)	10.6(0.8)	1.04(1.41)	129(18.5)	16,371(1286)	136(12.2)	432(39.2)	535(95.6)
CC T	9.45(0.24)	NA [a]	24.7(12.8)	0.03(0.06)	175(35.8)	10,547(5025)	140(12.9)	471(38.4)	4416(3457)
SS UT	6.81(0.06)	15.5(0.10)	216(34.3)	ND [b]	372(90.2)	1200(274)	1240(242)	190(27.0)	11,077(2985)
SS T	6.86(0.02)	NA	33.3(5.6)	ND	1285(19.6)	1015(163)	1683(313)	255(55.1)	4205(647)

[a] Not measured; [b] below the detection limit.

3.2. Plant Growth

In the absence of fertilizers, both the untreated and treated CC biochars had no effect on corn growth across all three growing cycles (Figure 1a–c). On the other hand, the untreated SS biochar (without fertilizer) more than tripled corn biomass compared to the unfertilized soil and was on par with the fertilized control in the first crop cycle (Figure 1d), but the positive effect did not persist through the 2nd and 3rd crop cycles (Figure 1e,f). The combination of biochar and fertilizer produced significant benefits to corn growth compared with the fertilizer alone treatments in the 1st and 3rd crop cycles. In the first crop, fertilizer+biochar combinations for both biochar types doubled corn growth (Figure 1a,d) and more than tripled growth in the 3rd crop for the SS biochars (Figure 1f).

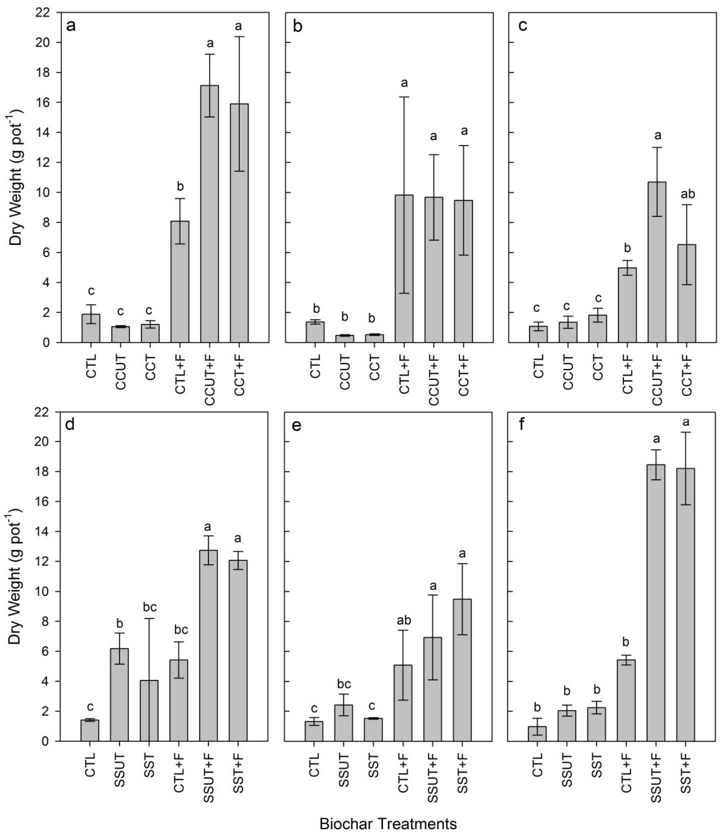

Figure 1. Corn cob biochar effects on corn above-ground dry matter production in crop cycle 1 (**a**); 2 (**b**); and 3 (**c**). Sewage sludge biochar effects on corn above-ground dry matter production in crop cycle 1 (**d**); 2 (**e**); and 3 (**f**).

3.3. Soil Properties

Biochar amendment had immediate and mostly beneficial effects on soil properties, but there were some important differences due to both biochar type and anaerobic treatment. Treating the two biochars increased their liming potential compared with their untreated counterpart raising pH by one unit to 7.00 for the treated CC biochar, but the improvement was smaller for the treated SS biochar (Table 3). Both CC biochars more than doubled soil C content with no treatment effect while the treated SS biochar was more effective at raising soil C. The larger increase in soil C from CC biochar amendment is a reflection of the high fixed C content of the CC biochar. Contrary to expectations, despite a much lower total N content, the CC biochars increased soil N content two-fold, but the high N SS biochars had no effect on soil N compared with the unamended soil. Both treated biochars significantly increased soil P and Mg above their untreated counterparts and the control soil. Both treated and untreated biochars increased soil Ca above the control, but showed no differences due to treatment. On the other hand, both biochars significantly increased soil K, but the untreated biochars showed the greatest effect.

There were noteworthy differences in how biochar type and treatment affected soil properties over the three crop cycles in relation to fertilization. In the absence of a fertilizer treatment, soil pH showed some increases in the control soil, an increase with the untreated CC biochar, and no change with the treated biochar. For the SS biochars there was a consistent drop in pH with the treated biochar, but only an initial drop with the untreated biochar from the first to second crops followed by no change. In the fertilized treatments, however, pH dropped consistently with each subsequent crop cycle and the decreases were more pronounced in the unamended soil where the pH dropped by more than one unit in the CC experiments and by approximately one unit in the SS experiments. Although the SS biochars were generally less effective in raising soil pH in comparison to the CC biochars, they appeared more effective at buffering the soil against the acidifying effects of the fertilizer. Soil pH decreases from the pre-plant to third harvest were 0.99, 0.28, and 0.51 for the control, untreated and treated SS biochars, respectively. For the CC experiments where pH decreases from fertilizer were more severe (1.62 units in the control soils), the untreated biochar reduced pH decline to 0.89 units, but its treated counterpart by 1.8 units.

Table 3. Biochar effects on selected soil chemical properties over three corn cropping cycles. Values are the means of four replicates where same letter within the same biochar type and cropping cycle denotes no significant difference (P < 0.05).

Treatment	pH	TC	TN	P	K	Ca	Mg
		$g \cdot kg^{-1}$			$mg \cdot kg^{-1}$		
Corn Cob Biochar							
Crop Cycle 1							
Control	6.16 ^{b}	12.6 ^{b}	1.5 ^{b}	8.31 ^{b}	427 ^{c}	686 ^{b}	219 ^{c}
Untreated	6.31 ^{b}	26.11 ^{a}	3.0 ^{a}	10.7 ^{b}	1083 ^{a}	768 ^{a}	258 ^{b}
Treated	7.00 ^{a}	27.2 ^{a}	3.2 ^{a}	16.8 ^{a}	849 ^{b}	812 ^{a}	296 ^{a}
Crop Cycle 2							
Control	6.33 ^{b}	NA	NA	6.50 ^{c}	377 ^{d}	714 ^{b}	248 ^{a}
Control + F	5.56 ^{d}	NA	NA	10.5 ^{bc}	316 ^{d}	709 ^{b}	242 ^{a}
Untreated	6.67 ^{a}	NA	NA	10.2 ^{bc}	926 ^{a}	904 ^{a}	245 ^{a}
Untreated + F	6.00 ^{c}	NA	NA	14.8 ^{ab}	704 ^{b}	660 ^{b}	236 ^{a}
Treated	6.99 ^{a}	NA	NA	10.0 ^{bc}	665 ^{b}	902 ^{a}	243 ^{a}
Treated + F	6.27 ^{bc}	NA	NA	21.6 ^{a}	551 ^{c}	694 ^{b}	247 ^{a}
Crop Cycle 3							
Control	6.53 ^{b}	11.7 ^{c}	1.3 ^{b}	7.54 ^{d}	154 ^{d}	754 ^{ab}	207 ^{ab}
Control + F	4.58 ^{d}	14.2 ^{c}	1.6 ^{b}	14.8 ^{bc}	222 ^{d}	650 ^{ab}	181 ^{ab}
Untreated	6.73 ^{b}	30.7 ^{a}	3.3 ^{a}	7.76 ^{d}	917 ^{a}	830 ^{a}	243 ^{ab}
Untreated + F	5.44 ^{c}	26.5 ^{b}	3.0 ^{a}	16.9 ^{ab}	393 ^{c}	531 ^{b}	150 ^{b}
Treated	7.08 ^{a}	29.6 ^{ab}	3.4 ^{a}	12.2 ^{c}	608 ^{b}	872 ^{a}	247 ^{a}
Treated + F	5.17 ^{c}	28.8 ^{ab}	3.3 ^{a}	19.6 ^{a}	347 ^{c}	544 ^{b}	162 ^{ab}
Sewage Sludge Biochar							
Crop Cycle 1							
Control	6.23 ^{b}	10.5 ^{c}	2.1 ^{a}	13.8 ^{b}	285 ^{c}	957 ^{b}	251 ^{c}
Untreated	6.07 ^{c}	15.7 ^{b}	1.8 ^{a}	24.1 ^{b}	434 ^{a}	1137 ^{a}	363 ^{b}
Treated	6.59 ^{a}	17.8 ^{a}	2.1 ^{a}	31.9 ^{a}	375 ^{b}	1092 ^{a}	385 ^{a}
Crop Cycle 2							
Control	6.40 ^{a}	NA	NA	8.88 ^{c}	184 ^{a}	835 ^{d}	227 ^{b}
Control + F	5.43 ^{c}	NA	NA	8.28 ^{c}	199 ^{a}	900b ^{c}	239 ^{b}
Untreated	5.82 ^{b}	NA	NA	30.0 ^{a}	211 ^{a}	945 ^{b}	351 ^{a}
Untreated + F	5.73 ^{b}	NA	NA	22.5 ^{b}	211 ^{a}	1055 ^{a}	367 ^{a}
Treated	6.32 ^{a}	NA	NA	32.7 ^{a}	237 ^{a}	875 ^{cd}	356 ^{a}
Treated + F	6.33 ^{a}	NA	NA	27.0 ^{ab}	263 ^{a}	980 ^{b}	365 ^{a}
Crop Cycle 3							
Control	6.33 ^{a}	13.2 ^{c}	1.5 ^{c}	6.48 ^{e}	193 ^{ab}	816 ^{b}	226 ^{d}
Control + F	5.24 ^{d}	14.2 ^{c}	1.6 ^{c}	16.5 ^{de}	98.3 ^{bc}	674 ^{c}	151 ^{e}
Untreated	5.89 ^{bc}	18.5 ^{b}	2.1 ^{b}	24.4 ^{cd}	160 ^{abc}	916 ^{a}	361 ^{b}
Untreated + F	5.79 ^{c}	26.5 ^{a}	2.1 ^{b}	58.8 ^{a}	68.4 ^{c}	850 ^{ab}	272 ^{c}
Treated	5.42 ^{d}	17.1 ^{b}	1.9 ^{b}	38.1 ^{bc}	205 ^{a}	909 ^{a}	396 ^{a}
Treated + F	6.08 ^{a}	28.8 ^{a}	3.2 ^{a}	52.4 ^{a}	80.3 ^{c}	911 ^{a}	339 ^{a}

In the absence of fertilizers, soil nutrient status showed a declining trend with cropping cycle with the exception of Ca, which increased in concentration under both CC biochar treatments and P and Mg, which also increased in the third cycle with the treated SS biochar. However, in combination with fertilizer, there were some notable differences in biochar type effects on soil nutrient status. While the CC biochar treatments showed an overall decline in soil nutrient status with the exception of soil P, the SS biochar treatments were more effective at buffering nutrient losses for K and Mg. Most notable were the increases in soil P and Mg content from the SS biochars over three cropping cycles. We also remark that the SS biochars showed lower declines in soil Ca (-77 mg· kg^{-1}) compared with the CC biochars (-253 mg· kg^{-1}). The treated SS biochar was especially effective at maintaining Ca and Mg in the soil whereas its untreated counterpart was more effective at enhancing soil P.

Soil C status showed only small changes over the three cropping cycles in the absence of fertilizer with a 0.46% increase in the untreated CC biochar treatment and a 0.07% loss in the SS treated biochar treatment. To the contrary, when fertilizer was combined with the SS biochar, soil C increased by almost 1.1% when the untreated and treated treatments were averaged. The increase in soil C is likely due to the large enhancement of biomass production, including below-ground biomass, from SS biochars in the third crop.

3.4. Nutrient Uptake

In the absence of fertilizer, significant biochar effects on nutrient uptake were limited to the first crop cycle, and were more prevalent in the SS treatments than the CC treatments; the treated CC biochar only improved N uptake whereas the untreated SS biochar increased all nutrient uptake except N and Fe (Table 4). In combination with fertilizer, the SS biochars remained more effective at enhancing nutrient uptake, especially in the third crop cycle. For the CC biochars both the treated and untreated biochars increased P uptake, the treated biochar increased Mg uptake, and the untreated biochar increased B and Cu uptake in the first crop. By the third crop, only the untreated CC biochar maintained positive effects on P, K, Mg, Cu and Zn uptake. For the SS, both the untreated and treated biochars increased nutrient uptake above the control + fertilizer, except for N and Mn, which were increased in the untreated SS biochar in the first crop cycle, and Ca, which increased in the treated biochar in the third crop cycle. The magnitude of biochar induced uptake was much higher for the SS in both cropping cycles, but improvements were especially remarkable in the third crop cycle where, for example, we observed a four-fold improvement for P and a three-fold increase for Mg above the control + fertilizer treatments. The improved corn nutrient uptake is generally matched by biochars' maintenance or enhancement of the respective nutrients in the soil. This is especially clear for P, where the SS biochars caused substantial increases in available soil P.

Table 4. Corn cob and sewage sludge biochar effects on elemental uptake into corn biomass in the first and third crop cycles. Means followed by same letter are not significantly different ($P < 0.05$) for comparisons made within each crop cycle (n = 4 per treatment).

Treatment	N	P	K	Ca	Mg	B	Cu	Fe	Mn	Zn
	mg· pot^{-1}					mg· pot^{-1}				
Corn Cob Biochar										
Crop Cycle 1										
Control	23.1 ^{b}	1.84 ^{c}	82.2 ^{c}	10.5 ^{b}	5.68 ^{c}	0.03 ^{c}	0.02 ^{c}	1.10 ^{ab}	0.33 ^{c}	0.08 ^{cd}
Control + F	228 ^{a}	14.2 ^{b}	493 ^{b}	47.9 ^{a}	28.8 ^{b}	0.11 ^{b}	0.08 ^{b}	1.33 ^{a}	4.54 ^{a}	0.44 ^{bc}
Untreated	18.6 ^{b}	3.92 ^{c}	44.9 ^{c}	4.93 ^{b}	4.11 ^{c}	0.02 ^{c}	0.005 ^{c}	1.23 ^{a}	0.18 ^{c}	0.07 ^{d}
Untreated + F	214 ^{a}	27.6 ^{a}	852 ^{a}	52.4 ^{a}	33.5 ^{ab}	0.16^{a}	0.11^{a}	1.23 ^{a}	1.94 ^{b}	2.37 ^{a}
Treated	15.6 ^{a}	4.59 ^{c}	68.9 ^{c}	4.90 ^{b}	4.55 ^{c}	0.03 ^{c}	0.005 ^{c}	0.05 ^{b}	0.21^{c}	0.07^{d}
Treated + F	205 ^{a}	21.8 ^{a}	777 ^{a}	52.7 ^{a}	37.6 ^{a}	0.13 ^{ab}	0.10 ^{ab}	1.63 ^{a}	1.84 ^{b}	0.69 ^{b}
Crop Cycle 3										
Control	4.88 ^{b}	0.79 ^{c}	36.5 ^{d}	4.05^{b}	2.92 ^{c}	0.01 ^{b}	0.004 ^{c}	1.31 ^{ab}	0.11 ^{c}	0.02 ^{b}
Control + F	138 ^{a}	7.38 ^{bc}	228 ^{bc}	26.9 ^{a}	18.3^{b}	0.09 ^{a}	0.042 ^{b}	3.61 ^{a}	8.94 ^{a}	0.36 ^{b}
Untreated	7.41 ^{b}	2.93 ^{c}	68.9 ^{d}	6.14 ^{b}	5.78^{c}	0.02 ^{b}	0.005 ^{c}	0.32 ^{b}	0.21 ^{c}	0.07 ^{b}
Untreated + F	213 ^{a}	20.7 ^{a}	446 ^{a}	34.4 ^{a}	29.2 ^{a}	0.13 ^{a}	0.075 ^{a}	1.16 ^{ab}	4.58 ^{b}	2.18 ^{a}
Treated	13.6 ^{b}	3.86 ^{c}	81.9 ^{cd}	6.61 ^{b}	7.17 ^{c}	0.03 ^{b}	0.006 ^{c}	0.19 ^{b}	0.24 ^{c}	0.09 ^{b}
Treated + F	178 ^{a}	14.3 ^{ab}	328 ^{ab}	24.3 ^{a}	21.8 ^{ab}	0.08 ^{a}	0.049 ^{ab}	0.65 ^{b}	4.34 ^{b}	0.42 ^{b}

Table 4. *Cont.*

Treatment	N	P	K	Ca	Mg	B	Cu	Fe	Mn	Zn
	mg· pot^{-1}					mg· pot^{-1}				
Sewage Sludge Biochar										
Crop Cycle 1										
Control	18.3 ^{d}	1.55 ^{c}	57.9 ^{c}	6.47 ^{c}	4.09 ^{c}	0.03 ^{c}	0.008 ^{c}	0.16 ^{b}	0.18 ^{d}	0.36 ^{d}
Control + F	177 ^{bc}	10.3 ^{bc}	284 ^{b}	20.6 ^{b}	14.9 ^{bc}	0.06 ^{bc}	0.05 ^{b}	1.97 ^{a}	1.07 ^{b}	0.24 ^{cd}
Untreated	96.5 ^{cd}	17.8 ^{b}	299 ^{b}	19.4 ^{bc}	20.1 ^{b}	0.07 ^{b}	0.04 ^{bc}	1.33 ^{ab}	0.77 ^{bc}	0.45 ^{bc}
Untreated + F	381 ^{a}	36.9 ^{a}	699 ^{a}	46.3 ^{a}	46.8 ^{a}	0.16 ^{a}	0.11 ^{a}	1.39 ^{ab}	3.30 ^{a}	1.32 ^{a}
Treated	59.1 ^{d}	15.0 ^{bc}	178 ^{bc}	15.3 ^{bc}	13.3 ^{bc}	0.05 ^{bc}	0.02 ^{bc}	0.27 ^{b}	0.34 ^{cd}	0.19 ^{cd}
Treated+F	251 ^{b}	33.2 ^{a}	585 ^{a}	37.2 ^{a}	36.4 ^{a}	0.14 ^{a}	0.08 ^{a}	1.15 ^{ab}	0.91 ^{bc}	0.68 ^{b}
Crop Cycle 3										
Control	11.2 ^{b}	1.08 ^{b}	37.4 ^{c}	4.66 ^{c}	3.08 ^{b}	0.02 ^{b}	0.004 ^{c}	0.15 ^{b}	0.09 ^{d}	0.02 ^{b}
Control + F	139 ^{a}	8.55 ^{b}	202 ^{b}	28.2 ^{b}	23.6 ^{b}	0.11 ^{b}	0.04 ^{b}	0.47 ^{ab}	1.94 ^{ab}	0.21 ^{b}
Untreated	18.7 ^{b}	7.36 ^{b}	83.2 ^{c}	7.81 ^{c}	10.7 ^{b}	0.07 ^{b}	0.006 ^{c}	0.06 ^{b}	0.31 ^{cd}	0.09 ^{b}
Untreated + F	207 ^{a}	36.5 ^{a}	311 ^{a}	45.0 ^{ab}	74.4 ^{a}	0.33 ^{a}	0.08 ^{a}	0.86 ^{ab}	2.63^{a}	0.89 ^{a}
Treated	20.4 ^{b}	8.64 ^{b}	92.9 ^{c}	6.86 ^{c}	9.98 ^{b}	0.05 ^{b}	0.007 ^{c}	0.10 ^{b}	0.16^{d}	0.09 ^{b}
Treated + F	190 ^{a}	39.2 ^{a}	307 ^{a}	52.2 ^{a}	79.4 ^{a}	0.34 ^{a}	0.08 ^{a}	1.43 ^{a}	1.32^{bc}	0.64 ^{a}

3.5. Heavy Metal Accumulation

Concentrations of As, Cd, Cr, and Pb in the above ground tissue of the corn plants were generally below maximum permitted concentrations established by WHO with the following exceptions: As concentration exceeded limits in untreated SS biochar treatment in the first crop and in the control in the third crop; Cd exceeded the limit in the control in the first crop (Table 5). For As, Ni, Pb and Se there were no significant biochar effects on above ground tissue concentrations compared with the control in both the first and third crop cycles. In the first crop, all biochar materials significantly reduced Cd concentration in the plant tissue whereas in the third crop the SS biochars were more effective in reducing Cd accumulation. Furthermore, in the third crop, all biochars caused a significant reduction in tissue Co concentration compared with the control. Finally, the treated SS biochar significantly reduced tissue Cr concentrations compared with the control in the first crop. With the exception of Cd, heavy metal uptake was not affected by biochar treatment (Table 5). The type of biochar affected Cu and Zn uptake into the corn biomass. For the CC biochar, the fertilized untreated material significantly promoted Cu and Zn uptake ($P < 0.05$) compared to the fertilized control in both the first and third crops while the treated CC biochar did not significantly affect uptake (Table 4). For the SS biochars, Cu and Zn uptake increased significantly in both the fertilized treated and untreated treatments compared with the control in both crop cycles.

Table 5. Sewage sludge biochar effects on heavy metal accumulation in above-ground corn biomass in fertilized treatments. Means followed by same letter are not significantly different ($P < 0.05$) for comparisons made within each crop cycle ($n = 4$ per treatment).

Treatment	As	Cd	Co	Cr	Ni	Pb	Se
Crop Cycle 1							
Tissue Concentration							
				mg· kg^{-1}			
Control	0.098 ^{a}	0.580 ^{a}	0.060 ^{ab}	0.374 ^{a}	0.214 ^{a}	0.331 ^{a}	0.054 ^{a}
CC UT	0.090 ^{a}	0.220 ^{b}	0.015 ^{b}	0.239 ^{ab}	0.191 ^{a}	0.183 ^{a}	0.204 ^{a}
CC T	0.087 ^{a}	0.264 ^{b}	0.019 ^{ab}	0.278 ^{ab}	0.129 ^{a}	0.199 ^{a}	0.530 ^{a}
SS UT	0.116 ^{a}	0.140 ^{b}	0.088 ^{a}	0.334 ^{ab}	0.206 ^{a}	0.173 ^{a}	0.302 ^{a}
SS T	0.093 ^{a}	0.188 ^{b}	0.044 ^{ab}	0.206 ^{b}	0.355 ^{a}	0.132 ^{a}	0.370 ^{a}
*WHO MPC **	*0.1*	*0.05-0.4*	*NA*	*1.0*	*NA*	*0.05–1.5*	*NA*

Table 5. *Cont.*

Treatment	As	Cd	Co	Cr	Ni	Pb	Se
Crop Cycle 1							
Elemental Uptake							
				$\mu g \cdot pot^{-1}$			
Control	0.79 [a]	4.66 [a]	0.49 [a]	3.02 [a]	1.72 [a]	2.65 [a]	0.44 [a]
CC UT	1.58 [a]	3.74 [abc]	0.28 [a]	4.07 [a]	3.23 [a]	3.13 [a]	3.33 [a]
CC T	1.40 [a]	3.94 [ab]	0.35 [a]	4.24 [a]	2.11 [a]	3.31 [a]	8.81 [a]
SS UT	1.50 [a]	1.85 [c]	1.16 [a]	4.36 [a]	2.76 [a]	2.34 [a]	3.98 [a]
SS T	1.17 [a]	2.22 [bc]	0.50 [a]	2.50 [a]	4.15 [a]	1.62 [a]	4.42 [a]
Crop Cycle 3							
Tissue Concentration							
				$mg \cdot kg^{-1}$			
Control	0.129 [a]	0.363 [a]	0.312 [a]	0.226 [a]	0.983 [a]	0.102 [a]	0.347 [a]
CC UT	0.089 [a]	0.194 [bc]	0.051 [b]	0.342 [a]	0.387 [a]	0.206 [a]	0.450 [a]
CC T	0.084 [a]	0.279 [ab]	0.108 [b]	0.325 [a]	0.359 [a]	0.117 [a]	0.584 [a]
SS UT	0.071 [a]	0.136 [cd]	0.037 [b]	0.243 [a]	0.161 [a]	0.178 [a]	0.437 [a]
SS T	0.082 [a]	0.056 [d]	0.256 [b]	0.285 [a]	0.440 [a]	0.117 [a]	0.375 [a]
Elemental Uptake							
				$\mu g \cdot pot^{-1}$			
Control	0.64 [a]	1.85 [a]	1.58 [a]	1.34 [a]	4.90 [a]	0.51 [a]	1.78 [a]
CC UT	0.89 [a]	2.00 [a]	0.50 [b]	3.62 [a]	4.12 [a]	2.04 [a]	5.11 [a]
CC T	0.58 [a]	1.77 [a]	0.66 [b]	2.05 [a]	2.16 [a]	0.82 [a]	4.38 [a]
SS UT	0.93 [a]	1.80 [a]	0.49 [b]	3.25 [a]	2.13 [a]	2.45 [a]	5.70 [a]
SS T	1.55 [a]	1.00 [a]	0.53 [b]	5.40 [a]	7.50 [a]	2.35 [a]	5.82 [a]

* Maximum permitted concentration [56].

4. Discussion

4.1. Plant Growth

Overall, results from the greenhouse experiments demonstrated significant biochar benefits to plant growth. The benefits were mostly observed when biochar materials were combined with fertilizer, except in the case of the untreated SS biochar, which produced plant growth comparable to the fertilized control in the first crop cycle only. For the sewage sludge biochars, increases of dry matter biomass relative to the control were higher than reported sewage sludge biochar effects on tomato [20,22] and similar to results reported for rice shoot weight [21]. By the third crop cycle, however, benefits from SS biochars were in excess of 250% compared with the chemical control, which is at the high end of reported growth responses to biochar [23].

Although biochar showed promise as a biofilm support increasing microbial activity in an anaerobic digestion system [41] and the anaerobically treated SS biochar showed a higher concentration of bioavailable macronutrients compared to its untreated counterpart, the nutrient enriched biochar produced no significant added benefit to plant growth in any of the greenhouse experiments. These results are in contrast to recent work showing that P-enriched biochar used in an anaerobic digestion system significantly improved early seedling germination and shoot growth [45].

Plant growth response to biochar application was related to improvements in soil nutrient status in the first crop cycle, and evidence for apparent alleviation of Mn toxicity, especially in the SS biochar treated soils in the third crop cycle. In the first crop cycle, results from regression analysis demonstrated that plant growth response to CC biochar treatments were significantly correlated to improvements in soil pH and extractable macronutrients (Figure 2). The CC biochar materials were effective at raising soil pH from near 6 to above 7 with a significant linear growth response up to about pH 6.5 (Figure 2a).

Corn growth showed a strong response to increasing P availability from biochar application, but the highest soil P concentrations achieved with the treated CC biochar application did not contribute to added plant growth (Figure 2b). Both the treated and untreated CC biochars more than doubled extractable K in the soils and contributed significantly to plant growth response (Figure 2c) with biochar derived Ca also contributing significantly to plant growth (Figure 2d). In addition to responses to changes in soil pH and extractable nutrients, plant growth response was also significantly related to decreases in tissue Mn concentration (Figure 3). For the SS biochar treatments in the first crop, plant growth responses were primarily explained by biochar derived increases in extractable base cation concentrations in the soil. The results for both biochar materials in our study agree with previous research demonstrating that direct contributions of mineral nutrients in the biochar ash component play an important role in remediating acidic soils and promoting plant growth [13,27,28,57–59].

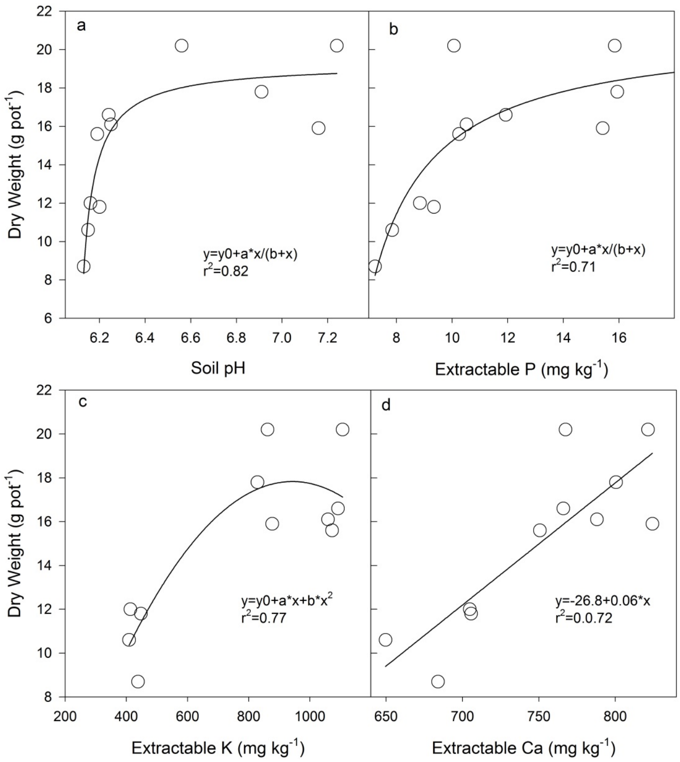

Figure 2. Corn above-ground dry weight biomass response to increasing soil pH (**a**); extractable P (**b**); K (**c**); and Ca (**d**) in control and biochar amended soils with fertilizer.

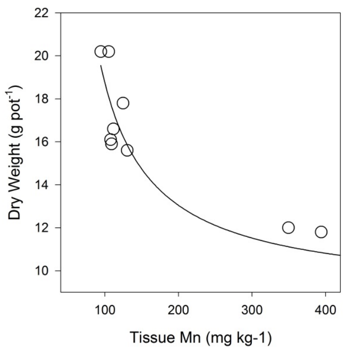

Figure 3. Above-ground corn dry weight biomass response to CC biochar treatments in the first crop cycle.

By the third crop cycle, we observed distinct differences in the effects of the two biochar materials. First, benefits to plant growth by the CC biochars were much reduced in the third crop with significant effects on growth limited to the untreated biochar. On the other hand, the SS biochars showed increasing benefits to plant growth over time and no differences between the treated or untreated biochars. Previous research has reported varying effects of time on biochar performance. In a greenhouse experiment evaluating the use of Flash Carbonized corn cob biochar applied to an acid Ultisol the benefits were short-lived and did not persist beyond the first crop cycle [27]. In contrast, a Flash Carbonized eucalyptus biochar showed no effect on plant growth in the first crop, but produced significant benefits to plant growth in the second crop [13]. At the field scale, there is some evidence that biochar benefits to crop growth are not realized in the first crop cycle, but take time to manifest themselves [60–62].

The persistence of a biochar liming effect controlling soil Mn bioavailability accompanied by improved nutrient availability were the primary drivers responsible for a positive plant growth response in the third crop; the effects were particularly notable in the SS biochar treated soils.

The SS biochar amended soils maintained a higher pH, which significantly reduced Mn bioavailability; plants in the unamended control exhibited toxic levels of Mn in the above-ground biomass (Figure 4a), which significantly inhibited plant growth compared with plants in the biochar treatments (Figure 4b). Both the treated and untreated biochars continued to provide a liming benefit with the treated biochar delivering significantly better liming power than its untreated counterpart. The liming value of sewage sludge biochars has been reported in previous research [21,22]. The biochar's liming potential significantly reduced Mn bioavailability lowering tissue Mn concentration more than fourfold compared with the control, and below the limit of 200 mg· kg^{-1} set for phytotoxicity in corn [53] (Figure 5a). Lower Mn in the aboveground tissue was the primary reason for higher yields in the biochar amended plots. Biochar-mediated liming reduced soil Mn solubility 5-fold in the untreated SS biochar and by more than 30-fold in its treated counterpart (Figure 5a). Low Mn concentrations in the saturated paste extract corresponded to low tissue Mn (Figure 6b) and much higher corn growth (Figure 5c). Recent greenhouse work reported that biochar alleviated Mn toxicity and improved corn growth in an Mn-rich Oxisol [13]. They attributed the remediation effect to improved Ca uptake with a reduction in Mn:Ca ratio in the plant tissue and organo-Mn complexation reactions inhibiting plant Mn uptake. Our results indicated that the high ash biochar directly detoxified Mn by reducing Mn solubility, but given the complexity of Mn reactions in soil, biochar mediated Mn detoxification merits further study.

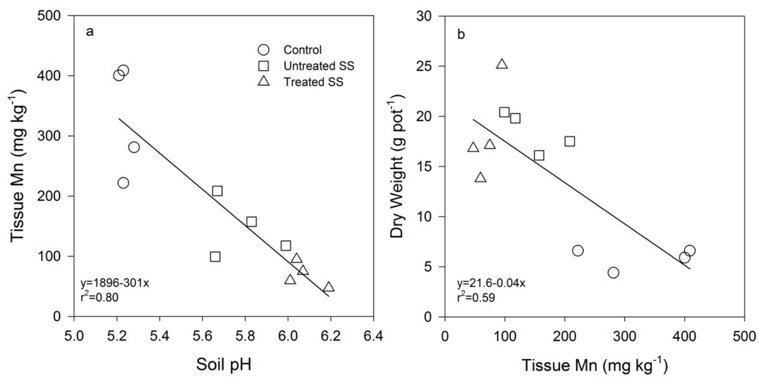

Figure 4. Sewage sludge biochar effects on soil pH and tissue Mn concentrations (**a**), and above-ground corn biomass (**b**), in relation to an unamended control (all treatments supplemented with fertilizer) in the third crop cycle.

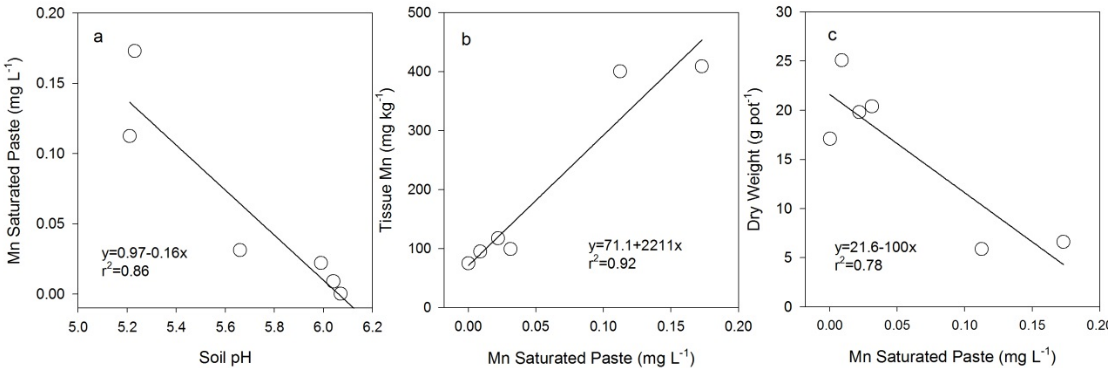

Figure 5. Sewage sludge biochar effects on soil pH and soil Mn concentrations (**a**); tissue Mn concentrations (**b**); and above-ground corn biomass (**c**) in relation to an unamended control (all treatments supplemented with fertilizer) in the third crop cycle.

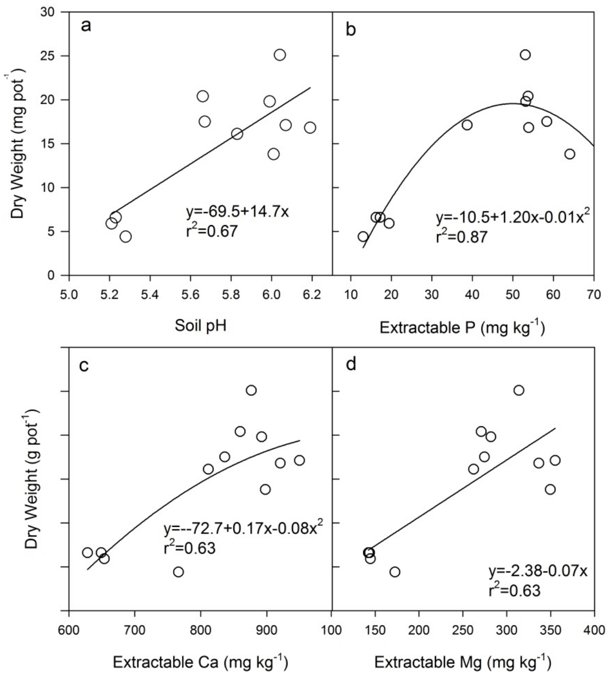

Figure 6. Sewage sludge biochar effects on soil pH (**a**); extractable P (**b**); Ca (**c**); and Mg (**d**) in relation to above-ground biomass in the third crop cycle.

In addition to its liming effect and associated detoxification of Mn, the SS biochars continued to supply essential nutrients through the third crop cycle contributing to improved plant growth. The maintenance of elevated soil pH, extractable P, Ca, and Mg corresponded to higher corn growth (Figure 6). We associate the persistence of a beneficial liming effect and elemental nutrient contribution promoting plant growth to the high ash content of the SS biochars in comparison to the lower ash CC biochars. The high P content of the SS biochars appeared to play an important role in promoting plant growth. The SS biochar amended soils showed a 4 to 6-fold increases in extractable soil P compared with the control soils, which corresponded to as much as a 4-fold increase in plant growth. These results agree with previous research demonstrating that biochars made from various feedstocks increase P solubility in soils [63] and serve as a slow-release form of P fertilizer [44,45,64]. A recent study utilizing a range of biochar materials showed that plant growth was highly correlated with P content of the biochar material with the high P sewage sludge biochar yielding the best plant growth response [19].

Overall, these results provide further evidence in support of the contention that agronomic benefits of biochar addition to soils are primarily associated with the ash component [23].

4.2. Heavy Metal Accumulation

Raw sewage sludge materials are typically high in pathogens and heavy metal concentrations making their application to land a potential source of contamination and hazardous to human health. Although carbonization of the raw feedstock tended to concentrate heavy metals in the biochar product, metal concentrations in the biochars did not exceed the ceiling concentration defined by the U.S. EPA [54] and the European Union (EU) [65]. However, when we consider the biochar loading rate in this series of experiments, levels of Cd, Cu, and Zn delivered by the SS biochars exceed the loading rates permitted by the EU. Therefore, in order to meet land application regulations, the SS biochar loading rates would need to be decreased by as much as 4-fold. According to regulations set by the State of Hawaii, the untreated CC and treated SS biochars exceeded the maximum allowable concentration for Mo, and both SS biochars exceeded the limits for Zn [55]. Thus, according to current regulations in the State of Hawaii, none of these biochars are permitted for land application. Similarly high Zn concentrations were measured in a number of sewage sludge biochars from various waste water treatment facilities [12,15,19,66,67].

There is a growing body of evidence demonstrating that sewage sludge biochars reduce heavy metal bioavailability in the soil and their accumulation in plants [14,20,21,68,69]. With the exception of Cd where the SS biochars significantly reduced plant uptake in the first crop cycle, our results showed no significant effect of biochars on heavy metal accumulation. Overall, metal concentrations in the corn tissue were below the WHO maximum permitted concentrations in the biochar amended soils. While these results do not support the general trend that biochar reduces metal availability, the lack of a significant effect compared to the control soils, from an agronomic perspective is important because it suggests that the sludge biochar is not a source of metal contamination for food crops allaying potential concerns from a food safety perspective.

5. Conclusions

Both the CC and SS biochars showed significant improvements to corn growth in combination with fertilizer in short term pot experiments. With fertilizer supplements, benefits to plant growth persisted and increased over the three cropping cycles in the SS biochar treated soils whereas benefits from the corn cob biochar were more short-term. Anaerobically treated biochars, enriched in essential plant nutrients, did not improve plant growth in comparison to their untreated counterparts except for the treated SS biochar, but its benefit did not persist beyond the first crop cycle. In addition to direct contributions of essential nutrients (P, Ca, Mg, K) from the ash-rich SS biochars, a persistent liming effect effectively countered the negative impacts of Mn toxicity brought about by the acidification of the soil from nitrogen fertilization.

Although the dramatic increases in plant growth with SS biochar amendments, coupled with no increase in heavy metal accumulation in crop biomass in the greenhouse bioassays, suggests that the pyrolytic conversion of sewage sludge into beneficial biochar is a potential alternative to the current practice of disposal in dwindling landfill space, the heavy metal concentration of the SS biochar remains problematic for land application. In addition, loading rates utilized in this experiment deliver excess Cd, Cu and Zn to the soil beyond some of the established regulatory limits. Despite these drawbacks, the evidence showing that thermal treatment of the sludge reduces heavy metal bioavailability is reason enough to continue exploring its use as a potentially beneficial soil amendment with a focus on application rates and metal bioavailability at the field scale. Of particular importance is the need to validate the persistence of biochar derived benefits over multiple crop cycles with just one application of the biochar material.

Supplementary Materials: The following are available online at http://www.mdpi.com/2071-1050/8/2/131/s1: Table S1: Deenik Supplemental Data.

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Author Contributions: Jonathan L. Deenik conceived and designed the experiments, performed data analysis, and drafted the manuscript. Michael J. Cooney conceived and designed experiments and edited the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

MDPI: Multidisciplinary Digital Publishing Institute
DOAJ: Directory of open access journals
TLA: Three letter acronym
LD: linear dichroism

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