



Article

The Sewage Sludge Biochar at Low Pyrolysis Temperature Had Better Improvement in Urban Soil and Turf Grass

Yanfang Tian, Liu Cui, Qimei Lin *, Guitong Li and Xiaorong Zhao

College of Resources and Environment, China Agricultural University, Beijing 100193, China; tyfang@cau.edu.cn (Y.T.); tlovebin@126.com (L.C.); lgtong@cau.edu.cn (G.L.); zhaoxr@cau.edu.cn (X.Z.)

* Correspondence: linqm@cau.edu.cn; Tel.: +86-1314-132-4624

Received: 29 January 2019; Accepted: 21 March 2019; Published: 25 March 2019



Abstract: In recent years, continuous efforts have been made to understand the impact of biochar on arable soil fertility. Little is known about whether the biochar derived from municipal sewage sludge has positive impacts on urban soil. In this study, we pyrolyzed spray-dried municipal sewage sludge at 200 °C, 300 °C, 500 °C, and 700 °C for 2 h in a muffle furnace and then amended it into an urban soil to grow turf grass in pots. The outcomes demonstrated that biochar incorporation caused remarkable increases in soil organic C, black C, total N, available P, and K by 3–8, 7–25, 2–9, 10–19, and 1.4–2 times, respectively. The dry matter of turf grass increased by 43–147%, probably due to the nutritional improvement after biochar addition. The turf grass grown in biochar-added soil had 4–70% lower heavy metals than that in the control, although the soils had much higher total heavy metals, which might imply that biochar amendment reduced the bioavailability of heavy metals. Considering the cost of biochar production and its impacts on both urban soil and grass, it would be alternative to convert the spray-dried municipal sewage sludge into biochar at 200 °C for 2 h and then used as an urban soil amendment.

Keywords: municipal sewage sludge; pyrolysis temperature; biochar; urban soil; turf grass

1. Introduction

Urban soils are mostly anthrosols and usually of poor structure and low fertility since they are seriously disturbed by human beings [1]. These soils often have characteristics that limit plant growth while the maintenance is costly as well [2]. Urban wastes and peat are usually used as soil conditioners to build up urban soil fertility in many countries [3]. However, peat resources in urban territories in China are limited and urban waste cannot fully meet the requirement to improve the poor conditions of urban soils [3]. It is therefore meaningful and valuable to seek new methods and materials to enhance urban soil fertility.

Municipal sewage sludge is the product of wastewater treatment plant. China annually produces over 13 million tons (dry weight) of municipal sewage sludge with a predicted annual increase rate of around 10% over recent ten years [4]. The massive volume of municipal sewage sludge is recognized as “a future waste problem” and draws a growing attention for some time. Municipal sewage sludge is usually rich in organic matter and mineral nutrients, such as phosphorus, potassium, nitrogen, and trace elements, and thus can be used for compost [5,6]. However, the sludge also contains a significant amount of pollutants such as heavy metals, pathogens, and organics, which may prohibit its amendment into soil [7]. A significant portion of the sludge, at least 20% of the total, is not properly disposed in China and causes acute sanitary, environmental and social issues [8]. Therefore, there is an urgent need to develop environmentally and economically acceptable novel approaches for the safe disposal and better utilization of municipal sewage sludge in many cities in China.

Pyrolysis is an alternative technology that is clean and cost-efficient for treating organic wastes [9]. Numerous studies have reported that pyrolysis treatment can completely kill pathogens, stabilize the heavy metals in municipal sewage sludge, and reduce the bioavailability of mineral nutrients [10]. Biochar is the solid byproduct of pyrolysis. Extensive researches have shown that biochar can notably improve soil chemical, physical, and biological properties [6,11]. The low density and porous structure of biochar may reduce soil bulk density while enhancing soil water retention capacity, soil aeration, and permeability [12,13]. The functional groups in biochar can not only improve soil nutrient use efficiency and cation exchange capacity (CEC) [14,15], but also reduce the bioavailability and mobility of pollutants in soils [16,17]. The ash in biochar can result in significant liming effect and reduction of soil acidity and toxicities of Mn^{2+} , Al^{3+} , and some other heavy metals [18]. A number of cereals, tubers, roots, and fibers show positive response to biochar addition in tropical, subtropical, and even temperate regions [19]. Moreover, biochar amendment is conducive to promoting carbon sequestration, enlarging soil carbon pools, and lessening the emission of greenhouse gas [20].

A number of factors such as biochar nature, application rates, soil types, and plant species, make biochars have different influences on soil and plants [21,22]. Among them, both biochar nature and addition ratio may largely decide the impacts of biochar amendment on soil and plant [9,23]. Numerous studies have shown that biochar properties such as pH, composition, surface charge, functional group, and even the heavy metals largely depend on pyrolysis conditions, especially the pyrolysis temperature [7,24,25]. Our previous pot experiment showed that the added quantities of sewage sludge biochar significantly influenced urban soil and turf grass, and 5% addition rate resulted in much better improvement in both urban soil and turf grass growth [23].

In this work, spray-dried municipal sewage sludge collected from a pilot plant was pyrolyzed at 200 °C, 300 °C, 500 °C, and 700 °C for 2 h, which indicated torrefaction, slight, middle, and heavy carbonization, respectively. The collected biochars were amended into an urban soil which had low fertility and poor structure, and then, turf grass was grown in pots. We hypothesized that these biochars produced at different pyrolysis temperatures differed in their capacities to improve the urban soil quality and turf grass as a result of their differences in physicochemical properties, and even reduced the potential risks of heavy metal bioaccumulation. The aims of this study were (1) to quantify the impacts of sewage sludge biochars produced at different temperatures on urban soil fertility and turf grass growth, (2) to compare the changes of heavy metals in urban soil and turf grass, and (3) to recommend a cost-effective and suitable temperature for producing sewage sludge biochar to be used as an urban soil amendment.

2. Materials and Methods

2.1. Biochar Preparation

Bulk portions of spray-dried sludge (<2 mm) from the Gaobeidian Wastewater Treatment Plant in Beijing were tightly filled into steel cylinders (height × inner diameter = 10.5 cm × 6.5 cm). Slow pyrolysis was performed at 200 °C, 300 °C, 500 °C, and 700 °C for 2 h with a heating rate of 10 °C min⁻¹. The collected biochars (<1 mm), named B200, B300, B500, and B700, respectively, were used for the pot experiment. Their basic properties are shown in Table 1, and the heavy metal contents were previously described by Ma et al. [10]. It was obvious that the sludge had high ash but low organic matter, and the slow pyrolysis treatment greatly changed the sludge's characteristics. Mercury (Hg) was not detectable in the biochar due to volatilization during pyrolysis. The residual heavy metals markedly increased up to 50% of the total when the temperature was higher than 300 °C. The oxidizable, reducible and acid-extractable heavy metals increased with the increasing pyrolysis temperature. High pyrolysis temperature thereby reduced the bioavailability of heavy metals, although it increased their concentrations.

Table 1. The characteristics of municipal sewage sludge and their biochars produced at 200 °C, 300 °C, 500 °C, and 700 °C for 2 h in a muffle furnace.

| Samples | Yield (%) | pH | EC ($\mu\text{S cm}^{-1}$) | C H O N | | | | Ash | C/N | Extractable K Extractable P $\text{NH}_4^+\text{-N}$ $\text{NO}_3^-\text{-N}$ | | | |
|-----------|-----------|--------|------------------------------|---------|-------|--------|--------|--------|--------|---|--------|----------|--------|
| | | | | % | | | | | | mg kg^{-1} | | | |
| Feedstock | 0.00 | 7.29b | 421.30e | 17.61b | 2.74e | 9.05d | 2.42c | 68.18a | 7.28a | 9437a | 910.3e | 3258.75e | 30.00d |
| B200 | 92.19c | 6.54a | 347.00d | 17.09b | 2.09d | 10.01e | 2.19c | 68.62a | 7.80a | 9559a | 364.4d | 533.51d | 0.10a |
| B300 | 81.66b | 7.20b | 114.77c | 19.72c | 1.79c | 5.76c | 2.59cd | 70.14b | 7.61a | 10351b | 235.8c | 119.28c | 1.97b |
| B500 | 67.80a | 8.70c | 73.77a | 15.26b | 0.73b | 3.28b | 1.73b | 79.00a | 8.82b | 12652c | 181.3b | 21.41b | 2.77c |
| B700 | 65.12a | 11.15d | 96.20b | 11.33a | 0.31a | 1.90a | 0.71a | 85.75c | 15.96c | 13401d | 126.7a | 12.72a | 2.72c |

Each column with the same lowercase letter is not significantly different at the 5% level among the feedstock and their biochars produced at different pyrolysis temperatures.

2.2. Soil

A typical urban soil was collected from the Science Park of the west campus of China Agricultural University. It is a loamy soil, and its properties are as follows: pH 8.40, electrical conductivity (EC) 164.70 $\mu\text{S cm}^{-1}$, Olsen-P 7.80 mg kg^{-1} , available K 64.22 mg kg^{-1} , soil organic carbon (SOC) 3.37 g kg^{-1} , total nitrogen (TN) 0.27 g kg^{-1} , and black carbon (BC) 0.67 g kg^{-1} . Most of the heavy metals were lower than the national limits for arable soil except Cd, but the used urban soil was contaminated by Cd which was showed in Table 2 [26].

Table 2. The fractions and total amounts of heavy metals in the tested urban soil (mg kg^{-1}).

| Fractions | Mn | Zn | Cu | Cr | Pb | As | Cd |
|------------------|--------|-------|-------|-------|-------|------|------|
| Acid-soluble | 16.36 | 0.63 | 0.03 | 0.08 | 0.44 | 0.00 | 0.01 |
| Oxidable | 27.85 | 0.42 | 0.64 | 0.82 | 0.09 | 0.42 | 0.00 |
| Reducible | 104.56 | 1.16 | 0.00 | 0.01 | 0.15 | 0.16 | 0.02 |
| Residual | 186.85 | 48.01 | 36.06 | 31.29 | 14.04 | 3.05 | 1.04 |
| Total | 335.61 | 50.22 | 36.74 | 32.19 | 14.72 | 3.63 | 1.07 |
| National limit * | None | 300 | 250 | 100 | 350 | 25 | 1.0 |

*: The national environmental quality standard for soils from GB15618-1995.

2.3. Pot Experiment

Our previous study showed that addition rates of sewage sludge biochar significantly influenced the urban soil and turf grass growth, and 5% addition rate resulted in much better improvement in both urban soil and turf grass growth [23]. In this study, portions of bulk soil (<2 mm), each about 1.2 kg, were weighed and then thoroughly mixed with the sewage sludge biochars of B200, B300, B500, or B700 at 5% (w/w) and urea (66.67 mg N kg^{-1}) in clay pots (inner diameter \times height = 13 cm \times 12 cm). Soil without biochar addition was used as a control (CK). All the treatments were replicated four times. Every pot was sown with around 0.27 g (roughly equal to 200 kg ha^{-1}) of mixed grass seeds of liberator *Poa pratensis* L., *Poa pratensis* L., *Nuglade Poa pratensis* L., and *midnight Poa pratensis* L. in the same proportions. The pots were buried in the ground with 2 cm remaining above the soil and maintained soil moisture at about 60% of the water holding capacity. The aboveground biomass was collected with a scissor when it grew to approximately 15–20 cm in height, three times in whole experiment. After being washed with deionized water, the grass was denatured at 105 °C for 2 h and then oven-dried at 60 °C for 24 h. The oven-dried grass was assayed for total phosphorus (TP), nitrogen (TN), potassium (TK), and heavy metals. At the end of experiment, soil samples were taken from each pot and then determined pH, EC, Olsen-P, available K, total N, organic carbon, black carbon, and heavy metals.

2.4. Analysis

The values of pH and EC in the biochars (biochar/water, 1:10) were determined with a pH meter and conductivity meter, respectively. The ash content was estimated via incineration method at 500 °C for 30 min and then 815 \pm 10 °C for 60 min [27]. The total carbon (C), nitrogen (N), and hydrogen (H) contents were determined by an elemental analyzer (Vario EL III, CHONS Elemental Analyzer, Elementar, Germany). The oxygen content was calculated as the difference between the ash and the sum of C, N, and H. Extractable phosphorus was extracted using 1 mol L^{-1} NaHCO_3 at pH 8.5 (1:4 ratio of biochar to water, w/v) and then measured by the ascorbic molybdate blue spectrometry, while Extractable potassium was measured by flame photometry following extraction with a neutral 1 mol L^{-1} NH_4OAc solution [28]. Both ammonium and nitrate were extracted with neutral 1 mol L^{-1} KCl (biochar/water, 1:10, w/v) and then analyzed by a continuous flow auto analyzer (Auto Analyzer 3, Seal, Southampton, UK).

Total P of the turf grass was measured by ascorbic molybdate blue spectrometry after digestion with $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$, total N was determined by Kjeldahl method, and total K was measured by flame photometry. The heavy metals concentrations were analyzed using $\text{HClO}_4\text{-HNO}_3$ digestion followed by inductively coupled plasma spectrometry (ICP 6000 SERIES; Thermo Company, Rockford, IL, USA).

Soil pH values were determined by an ion selective electrode at 1:2.5 (soil/water, *w/v*), and EC was measured by a conductivity meter (soil/water, 1:5 *w/v*). Soil organic carbon and total nitrogen were measured by the potassium dichromate volumetric method and the Kjeldahl method respectively. Black carbon was determined by the benzene polycarboxylic acid (BPCA) method [29]. Available P and K were analyzed by the ascorbic molybdate blue spectrometry method and flame photometry method respectively.

Heavy metals in soil samples were obtained after digestion with $\text{HCl-HNO}_3\text{-HClO}_4$ and analyzed by inductively coupled plasma spectrometry. The heavy metals fractions were analyzed by the sequential extraction procedure of Bureau Commune de Reference [23]. In brief, 1 g of sample in a polypropylene centrifuge tube was thoroughly shaken with 30 mL of CH_3COOH (0.11 mol L^{-1} , pH 2.8) for 16 h at room temperature. The supernatant was considered to be the acid-soluble fraction. The residue was digested by hydroxylamine hydrochloride (0.1 mol L^{-1} , 20 mL) for 16 h at room temperature. This supernatant was the reducible fraction. The remaining material was digested with 5 mL H_2O_2 (pH 2) for 1 h at room temperature and then dried in the $80 \text{ }^\circ\text{C}$ water for 1 h. This was dissolved in 25 mL of NH_4OAc (0.1 mol L^{-1} , pH 2) solution for 16 h at room temperature and then filtered. The filtrate was considered to be the oxidable fraction. The difference between the total mass and the sum of the oxidable, acid-soluble, and reducible fractions was considered to be the residual fraction.

2.5. Statistical Analysis

All the data are expressed on an oven-dried basis as the mean of four replicates. Variance analysis was implemented by a one-way ANOVA and expressed as Duncan comparisons if the variation was significant at 95% confidence intervals.

3. Results

3.1. Soil Basic Chemical Characteristics

The sewage sludge biochar amendment induced substantial changes to most of the soil chemical parameters (Table 3). The pH values of the soils amended with B200, B300, and B500 decreased by 0.14–0.21 units, while no change was observed with amendment of B700, compared with that of the CK soil. Soil organic C, black C, total N, available P, and K increased by 3–8, 7–25, 2–9, 10–19, and 1.4–2 times, respectively, following biochar amendment. The proportion of black C in the total organic C increased by 9–272%. The ratios of organic C to total N (C/N) increased from 16.88 in CK to 26.39 in B700, while others decreased to 12.30–14.73. The biochars produced at low temperature (e.g., B200) tended to have higher positive impacts on the parameters such as available P and K and total N than that produced at high temperature (e.g., B700).

Table 3. The chemical properties of the soils amended with the biochars derived from municipal sewage sludge at 200 °C, 300 °C, 500 °C, and 700 °C for 2 h in a muffle furnace and then grown turf grass.

| Treatments | pH | EC | Organic C | Black C | BC in | Total N | C/N | Available | Available |
|------------|-------|-----------------------|--------------------|---------|--------------------|---------|--------|-----------|-----------|
| | | $\mu\text{S cm}^{-1}$ | g kg^{-1} | OC (%) | g kg^{-1} | P | | K | |
| CK | 8.77b | 83.74ab | 5.57a | 0.49a | 8.80a | 0.33a | 16.88b | 4.83a | 75.99a |
| B200 | 8.56a | 84.20ab | 38.24c | 3.67b | 9.60b | 3.11b | 12.30a | 92.87e | 169.90c |
| B300 | 8.63a | 79.38ab | 45.07d | 7.55c | 16.75c | 3.06b | 14.73a | 59.03c | 108.30b |
| B500 | 8.58a | 77.00a | 37.69c | 12.34d | 61.93e | 2.68b | 14.06a | 80.52d | 162.96c |
| B700 | 8.77b | 85.60b | 19.00b | 5.16b | 27.16d | 0.72a | 26.39c | 46.37b | 117.36b |

Each column with the same lowercase letter is not significantly different at the 5% level. C/N indicates the ratio of soil organic C to total N.

3.2. Soil Heavy Metals

The biochar-added soils generally had significantly higher heavy metals content than CK, which was obviously attributable to the added biochars (Table 4). In particular, the biochar-amended soils had 53–57%, 33–61%, and 13–35% higher Zn, Cu, and As, respectively than CK. The B300-amended soil even had up to 1.56 mg kg⁻¹ Cd, 15% higher than CK.

Table 4. Total quantities of the heavy metals in the soils amended with the biochars derived from municipal sewage sludge at 200 °C, 300 °C, 500 °C, and 700 °C for 2 h in a muffle furnace and then grown turf grass (mg kg⁻¹).

| Treatments | Mn | Zn | Cr | Cu | Pb | As | Cd |
|------------------|---------|---------|---------|--------|--------|-------|--------|
| CK | 400.75a | 65.13a | 41.54ab | 22.59a | 19.04a | 2.29a | 1.33a |
| B200 | 448.23b | 118.90b | 39.30a | 51.03c | 22.63b | 3.07b | 1.49bc |
| B300 | 442.14b | 123.63c | 42.63b | 38.09b | 22.69b | 2.89b | 1.56c |
| B500 | 418.77a | 137.84d | 44.20b | 58.22d | 21.66b | 3.53c | 1.40b |
| B700 | 434.36b | 116.21b | 38.07a | 33.84b | 21.02b | 2.62a | 1.32a |
| National limit * | None | 300 | 250 | 100 | 350 | 25 | 1.0 |

*: The national environmental quality standard for soils from GB15618-1995. Each column with the same lowercase letter is not significantly different at the 5% level among the treatments.

Residual heavy metals accounted for 44–100% of the total heavy metals in all the soils, following by the oxidable and reducible fractions with 0–23% and 0–39% of the total, respectively. The most active fractions of the acid soluble heavy metals comprised 0–15.62% of the total heavy metals (Figure 1). The heavy metals of Zn, Cr, Cu, Pb, and Cd had much higher residual fractions, more than 90%, but lower acid soluble fractions, while both Mn and As had much lower residual fractions, 63–80% of the total. Biochar amendment induced diverse impacts on the fractions of heavy metals, which were largely dependent on both heavy metals and the added biochars (Figure 1). The acid soluble fractions of Pb, Cd, and As were reduced by 38–100% following the biochar addition, while those of Mn, Zn, Cr, and Cu increased by 0.35–34 times. The reducible fractions of Pb and Cu decreased by 29–96% and 82–98%, respectively, while those of Zn, As, and Cd increased by 58–337%, 4–538%, and 2–223%, respectively. Furthermore, the biochar amendment increased the oxidable fraction of Pb by 82–100% but decreased that of Cd by 33–97%. In general, adding biochar produced in high temperatures, such as B700 induced an increase in more bioavailable fractions of heavy metals, while the biochar produced in low temperature biochar, such as B200 functioned more effectively to reduce those fractions.

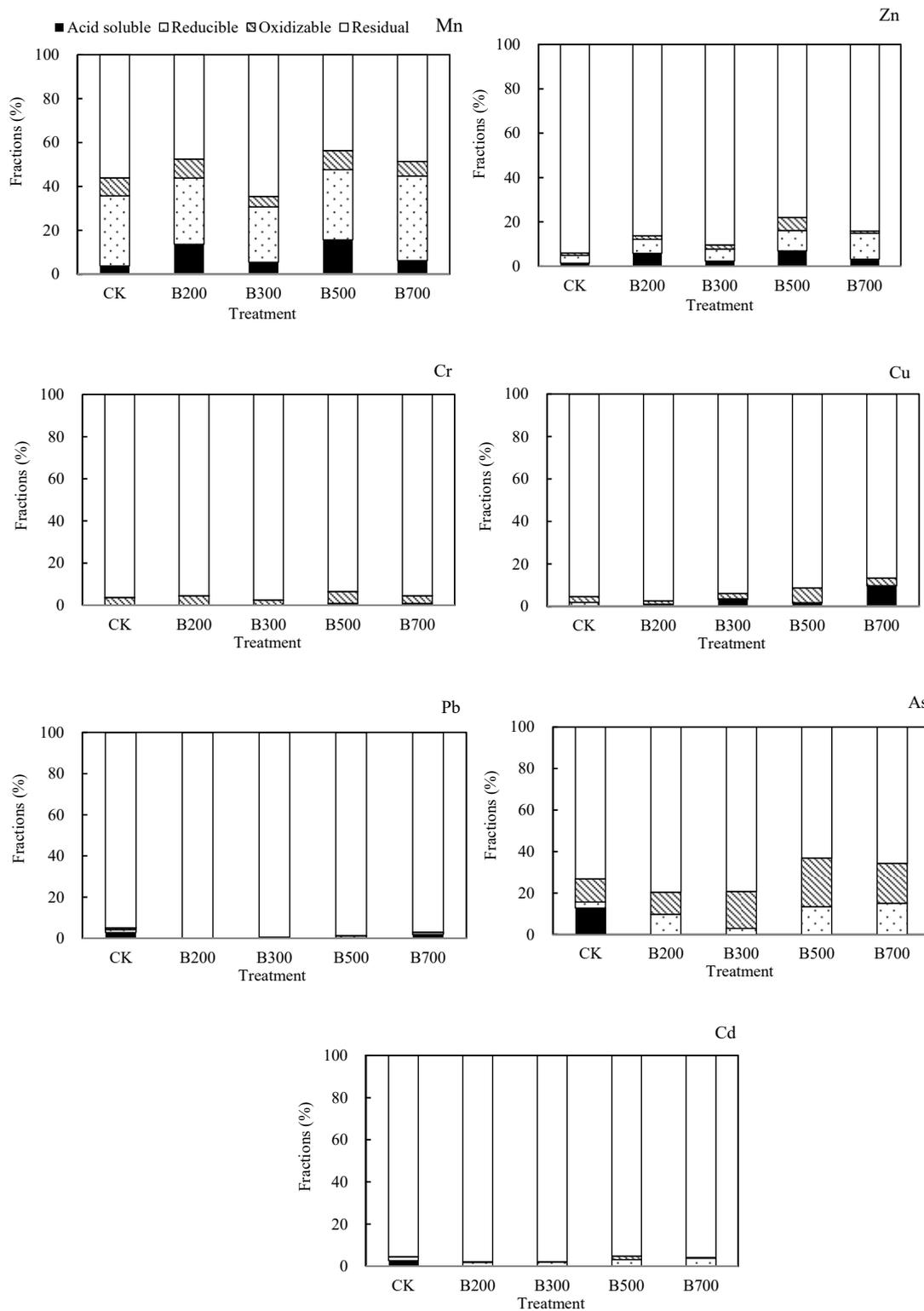


Figure 1. The percentages of different fractions in total amount of heavy metals in the soils amended with the biochars derived from municipal sewage sludge at 200 °C, 300 °C, 500 °C, and 700 °C for 2 h in a muffle furnace and then grown turf grass.

3.3. Turf Grass Biomass, NPK, and Heavy Metals

Biochar amendment had significant impacts on turf grass dry matter, nutrition, and heavy metals (Table 5). The dry matter of turf grass increased by 43–147% following the addition of the biochars

produced at low temperature but reduced by 12% with the addition of B700. The nutrients of NPK in the turf grass were significantly improved by the biochar amendment. The turf grass grown in biochar-amended soils had 27–58% and 3–43% more P and K, respectively, compared with that in CK. The biochar produced in low temperature showed much better improvement in the NPK nutrition of the turf grass than the biochar produced in high temperature. Compared with the other biochar, B200 significantly increased the N and K content of the turf grass. Arsenic concentration in the turf grass grown in either biochar-amended or biochar-free soils was not in the detectable range. However, biochar addition significantly reduced the accumulation of Mn, Zn, Cr, Cu, Pb, and Cd in the turf grass aboveground by 4–70%. The turf grass grown in the biochar-amended soils had 28–83% lower Cd content than that in the biochar-free soil. Both B200 and B500 induced lower absorption of heavy metals by turf grass than B300 and B700, and even the absorption of Cr by the turf grass grown in B200 was much lower than that of B500.

Table 5. The dry matter, NPK and heavy metals of the grass grown in the soils amended with the biochars derived from municipal sewage sludge at 200 °C, 300 °C, 500 °C, and 700 °C for 2 h in a muffle furnace.

| Treatments | Dry Matter | N | P | K | Mn | Zn | Cr | Cu | Pb | Cd |
|------------|------------|-------|-------|---------------------|--------|--------|-------|-------|-------|-------|
| | g/pot | % | | mg kg ⁻¹ | | | | | | |
| CK | 9.66a | 2.10a | 0.26a | 1.16a | 70.77d | 32.77d | 7.73c | 6.03d | 2.78c | 0.15d |
| B200 | 23.88c | 2.92b | 0.33b | 1.66d | 58.37c | 21.40b | 3.38a | 4.86c | 1.32a | 0.09b |
| B300 | 15.51b | 2.19a | 0.35b | 1.37c | 43.62b | 25.81c | 7.33c | 4.45c | 2.39b | 0.12c |
| B500 | 13.79b | 1.93a | 0.41c | 1.28bc | 27.99a | 15.70a | 4.21b | 2.22a | 1.15a | 0.04a |
| B700 | 8.48a | 2.10a | 0.36b | 1.20ab | 52.73c | 30.53d | 7.42c | 3.13b | 3.05c | 0.11c |

The different lowercase letters in the same column indicate a significant difference at $p < 0.05$ among the different treatments.

4. Discussion

4.1. Urban Soil Improvement Following Sewage Sludge Biochar Addition

Urban soil, definitely disturbed land, often contains stones, concrete, brick, and plastic, and has poor structure and low nutrients [30]. It is therefore a great challenge to establish and maintain vegetation in this soil [2]. A large amount of peat, compost, and mineral fertilizer is often used to improve urban soil [3]. Our results show that the biochar-added soils have much higher organic C, total N, and available N, P, and K compared with the soil without biochar amendment. The increased nutrients might be caused partially by the added biochar (Table 1) and partially by the increased nutrient retention capacity in the biochar-added soil [31]. For example, the lower total N in the sewage sludge biochar at high pyrolysis temperature (B700) resulted in less increase in soil total N following biochar addition. Similar results were reported by other researchers [7,32]. The much higher organic C in the biochar-amended soils than in CK could be explained by both the increase of grass residues and the added biochar. Furthermore, the inconsistency between the measured black C and the added biochar C would be interpreted as the decomposition and losses of the added biochar during the pot experiment [33,34]. Our results indicated the remarkable improvement of the tested urban soil through biochar amendment. These results were consistent with previous research findings [35,36]. The biochar produced at low temperatures showed higher positive impacts on urban soil improvement than those produced at high temperature. Agrafioti et al. [24] obtained similar results and suggested biochar produced at low temperature could be more suitable to agricultural use rather than that derived from high temperature. Considering the more volatile loss and bioavailability reduction of mineral nutrients at high pyrolysis temperatures [37], it may be thus recommended that municipal sewage sludge be converted into biochar at low temperature, e.g., 200 °C, and then used as a nutrient supplement for urban soil. Moreover, a few studies have shown that the biochar derived from lignocellulosic materials has the ability to ameliorate soil physical parameters such as pore size, proportion of water-stable

aggregates, bulk density, water retention, etc. [38,39]. The future work should be concerned on the impacts of municipal sewage sludge biochar on soil porosity, aggregates, permeability, infiltration, and hydrological characters.

4.2. The Impacts of Sewage Sludge Biochar Amendment on Soil Heavy Metals

Municipal sewage sludge often contains a significant amount of heavy metals, which restricts its agricultural utilization [40]. Slow pyrolysis could completely remove mercury through volatilization and greatly reduce the bioavailability of other heavy metals, although their concentrations could significantly increase [10]. Similar results were obtained by many researchers [7,41], possibly because the weight loss of the heavy metals is much lower than the that of organic compounds, thus resulting in the enrichment of heavy metals in biochar [41,42]. It was therefore reasonable that biochar amendment resulted in a proportional increase in total heavy metals (Table 4). The cadmium content even surpassed the national standards [16] and thus might entail some risk [43].

The fractions of heavy metals, and not the total amounts, are usually believed to have a much closer association with their bioavailability. A few reports have shown that biochar amendment may induce various changes in the fractions of soil heavy metals, which often depends on the added biochar, heavy metals, and soil conditions [44,45]. In this study, amending sewage sludge biochars led to remarkable reductions in acid soluble Pb, As, and Cd, reducible Cu and Pb, and oxidable Pb, but also led to increases in acid soluble Mn, Zn, and Cu, reducible Zn, As, and Cd, and oxidable As (Figure 1). It is believed that acid-soluble, oxidable, and reducible fractions of heavy metals have higher bioavailability [46]. Sewage sludge biochar amendment may therefore enhance the bioavailabilities of Mn, Zn, and Cu but reduce those of Pb, As, and Cd. Yue et al. [23] obtained similar results in both laboratory incubations and pot tests. Biochar effects on soil heavy metals fractions are not fully understood. The electrostatic attraction may cause an increase of exchangeable heavy metals since biochar carries a significant amount of charges [47]. The carbonates, phosphates, and oxides in biochar can result in the precipitation of heavy metals, which enhances the relative fractions of heavy metals in the biochar-added soil [48]. The different functional groups, for instance, carboxyls, phenolics, and hydroxyls, on the surface of porous biochar can adsorb heavy metals through coordination and chelation, which explains the improvements in acid-soluble, oxidable heavy metals in the biochar-added soils [43,44,49,50]. The microbial decomposition of biochar may decrease oxidable heavy metals and valence alteration of some heavy metals, for example, Cu, Cr, Mn, and As [51]. More work is obviously required to understand how biochar drives changes in the bioavailability of heavy metal fractions and the impacts on the environment.

4.3. Improvement of Turf Grass Following Sewage Sludge Biochar Amendment

Various studies have confirmed that biochar as a kind of soil amendment that can obviously enhance plant nutrition, stimulate plant growth, and improve grain yield and biomass [52,53]. We acquired similar outcomes in this research, in which biochar amendment significantly enhanced the dry matter and NPK nutrients of the turf grass. The biochar produced at lower temperature (e.g., B200) had much better improvement in turf grass for its higher available minerals, such as N, P, and K. The better growth of turf grass in the biochar-added urban soil might be largely attributed to the improvement in mineral nutrition. Similar results were reported by other researchers when they used high ash biochars rather than those with low ash [9].

The transfer of heavy metals from soil to crops is a public concern because of its potential health risks. A number of studies have shown that crops such as cherry tomato fruits [53], Chinese cabbages and radishes [54], turf grass [23], and garlic [43] grown in biochar-amended soil have lower heavy metals content than those in biochar-free soil. We obtained comparative outcomes in this study. The turf grass from the soils added with different sewage sludge biochars had much lower heavy metals than that from CK, though the soils amended with biochar had higher total heavy metals. This finding confirms that the total heavy metals quantity in soil is not often closely

equal to their bioavailabilities [55], and the bioavailability of heavy metals are generally controlled by the soil adsorption and desorption characteristics [56] which are reported to be related to soil properties [57]. Moreover, the adsorbed heavy metals in roots may not be transferred to aboveground tissues [58]. Lu et al. [59] demonstrated that insoluble metal phosphates inside root tissues inhibited metal migration from root to aboveground. The much lower heavy metals in the turf grass grown in both B200 and B500 than those in B300 and B700 may imply the complexity of transformation, absorption and transfer of heavy metals in the biochar-amended soils.

5. Conclusions

Spray-dried municipal sewage sludge could be effectively converted into biochar by a slow pyrolysis process within 200 °C–700 °C for 2 h. These biochars had specific characters which changed with pyrolysis temperature. The urban soils amended with the biochars had much higher values of organic C, N, P, and K compared with the control. The biochar amendment resulted in high turf grass biomass and NPK contents. It was evident that the biochar amendment could remarkably improve urban soil fertility and then promote turf grass growth. The biochar-amended soil had much higher total heavy metals than the control because of the input of biochar. However, the grass grown in biochar-amended soil accumulated less heavy metal than that in control, which might imply biochar amendment effectively reduced the bioavailability of heavy metals. In consideration of the economic factors and the positive impacts on soil and turf grass, it is recommended that the sewage sludge can be converted into biochar at 200 °C for 2 h and then used as a potential conditioner for urban soil.

Author Contributions: Conceptualization, Q.L.; Y.T.; Methodology, Q.L.; Y.T.; and L.C.; Software, Q.L.; Y.T.; Validation, Q.L.; G.L.; and X.Z.; Formal analysis, Q.L.; Y.T.; Investigation, Q.L.; Y.T.; and L.C.; Resources, Q.L.; G.L. and X.Z.; Data curation, Q.L.; Y.T. and L.C.; Writing—original draft preparation, Y.T.; Writing—review and editing, Q.L.; Visualization, Y.T.; Supervision, Q.L.; G.L.; and X.Z.; Project administration, Q.L.; G.L.; and X.Z.; Funding acquisition, Q.L.; G.L.; and X.Z.

Funding: This study was funded by the National Key Technology R&D Programme (No. 2015BAD05B03) and was implemented at the Key Laboratory of Arable Land Conservation (North China), Ministry of Agriculture, Key Laboratory of Plant-Soil Interactions, Ministry of Education, and China Agricultural University.

Acknowledgments: The authors would like to thank Wu for the reasonable management and arrangement of the experimental equipment.

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

References

1. Foti, L.; Dubs, F.; Gignoux, J.; Lata, J.C.; Lerch, T.Z.; Mathieu, J.; Nold, F.; Nunan, N.; Raynaud, X.; Abbadie, L.; et al. Trace element concentrations along a gradient of urban pressure in forest and lawn soils of the Paris region (France). *Sci. Total Environ.* **2017**, *598*, 938–948. [[CrossRef](#)]
2. Miao, F.; Shi, H. Analysis on the status of urban green land and its improvement measures (Chinese with English abstract). *Chin. Hortic. Abstr.* **2015**, *6*, 71–73.
3. Diaz, E.; Roldán, A.; Lax, A.; Albaladejo, J. Formation of stable aggregates in degraded soil by amendment with urban refuse and peat. *Geoderma* **1994**, *63*, 277–288. [[CrossRef](#)]
4. Havukainen, J.; Zhan, M.X.; Dong, J.; Liikanen, M.; Deviatkin, I.; Li, X.D.; Horttanainen, M. Environmental impact assessment of municipal solid waste management incorporating mechanical treatment of waste and incineration in Hangzhou, China. *J. Clean. Prod.* **2017**, *141*, 453–461. [[CrossRef](#)]
5. Tian, Y.; Zhang, J.; Zuo, W.; Chen, L.; Cui, Y.; Tan, T. Nitrogen conversion in relation to NH₃ and HCN during microwave pyrolysis of sewage sludge. *Environ. Sci. Technol.* **2013**, *47*, 3498–3505. [[CrossRef](#)] [[PubMed](#)]
6. Uchimiya, M.; Wartelle, L.H.; Klasson, K.T.; Fortier, C.A.; Lima, I.M. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. *J. Agric. Food Chem.* **2011**, *59*, 2501–2510. [[CrossRef](#)]
7. Yuan, H.R.; Lu, T.; Huang, H.Y.; Zhao, D.D.; Kobayashi, N.; Chen, Y. Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge. *J. Anal. Appl. Pyrolysis* **2015**, *112*, 284–289. [[CrossRef](#)]

8. Yue, Y.; Yao, Y.; Lin, Q.M.; Li, G.T.; Zhao, X.R. The change of heavy metals fractions during hydrochar decomposition in soils amended with different municipal sewage sludge hydrochars. *J. Soils Sediments* **2016**, *17*, 736–770. [[CrossRef](#)]
9. Luo, Y.; Jiao, Y.J.; Zhao, X.R.; Li, G.T.; Zhao, L.X.; Meng, H.B. Improvement to maize growth caused by biochars derived from six feedstock prepared at three different temperatures. *J. Integr. Agric.* **2014**, *13*, 533–540. [[CrossRef](#)]
10. Ma, T.; Song, Y.H.; Li, G.T.; Zhao, X.R.; Lin, Q.M. Characteristics of the form and concentration of heavy metals in the biochar made from municipal sewage sludge (Chinese with English abstract). *J. China Agric. Univ.* **2013**, *18*, 189–194.
11. Gaskin, J.W.; Steiner, C.; Harris, K.; Das, K.C.; Bibens, B. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans. ASABE* **2008**, *51*, 2061–2069. [[CrossRef](#)]
12. Ajayi, A.E.; Holthusen, D.; Horn, R. Changes in microstructural behaviour and hydraulic functions of biochar amended soils. *Soil Tillage Res.* **2016**, *155*, 166–175. [[CrossRef](#)]
13. Alfred, O.; Mulder, J.; Martinsen, V.; Cornelissen, G.; Børresen, T. In situ effects of biochar on aggregation, water retention and porosity in light-textured tropical soils. *Soil Tillage Res.* **2016**, *155*, 35–44.
14. Jien, S.H.; Wang, C.S. Effects of biochar on soil properties and erosion potential in a highly weathered soil. *Catena* **2013**, *110*, 225–233. [[CrossRef](#)]
15. Prapagdee, S.; Tawinteung, N. Effects of biochar on enhanced nutrient use efficiency of green bean, *Vigna radiata* L. *Environ. Sci. Pollut. Res.* **2017**, *24*, 9460–9467. [[CrossRef](#)]
16. Bielská, L.; Škulcová, L.; Neuwirthová, N.; Cornelissen, G.; Hale, S.E. Sorption, bioavailability and ecotoxic effects of hydrophobic organic compounds in biochar amended soils. *Sci. Total Environ.* **2018**, *624*, 78–86. [[CrossRef](#)] [[PubMed](#)]
17. Mohamed, B.A.; Ellis, N.; Kim, C.S.; Bi, X.T. The role of tailored biochar in increasing plant growth, and reducing bioavailability, phytotoxicity, and uptake of heavy metals in contaminated soil. *Environ. Pollut.* **2017**, *230*, 329–338. [[CrossRef](#)] [[PubMed](#)]
18. Al-wabel, M.I.; Usman, A.R.A.; El-naggar, A.H.; Aly, A.A.; Ibrahim, H.M.; Elmaghraby, S.; Al-Omran, A. Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. *Saudi J. Biol. Sci.* **2015**, *22*, 503–511. [[CrossRef](#)]
19. Biederman, L.; Harpole, W.S. Biochar and its effects on plant productivity and nutrient cycling—A meta-analysis. *GCB Bioenergy* **2013**, *5*, 202–214. [[CrossRef](#)]
20. Wu, H.P.; Lai, C.; Zeng, G.M.; Liang, J.; Chen, J.; Xu, J.J.; Dai, J.; Li, X.D.; Liu, J.F.; Chen, M.; et al. The interactions of composting and biochar and their implications for soil amendment and pollution remediation: A review. *Crit. Rev. Biotechnol.* **2017**, *37*, 754–764. [[CrossRef](#)] [[PubMed](#)]
21. Ding, Y.; Liu, Y.G.; Liu, S.B.; Li, Z.W.; Tan, X.F.; Huang, X.X.; Zeng, G.M.; Zhou, L.; Zheng, B.H. Biochar to improve soil fertility. A review. *Agron. Sustain. Dev.* **2016**, *36*, 36. [[CrossRef](#)]
22. Jones, D.L.; Rousk, J.; Edwards-Jones, G.; DeLuca, T.H.; Murphy, D.V. Biochar-mediated changes in soil quality and plant growth in a three year field trial. *Soil Biol. Biochem.* **2012**, *45*, 113–124. [[CrossRef](#)]
23. Yue, Y.; Cui, L.; Lin, Q.M.; Li, G.T.; Zhao, X.R. Efficiency of sewage sludge biochar in improving urban soil properties and promoting grass growth. *Chemosphere* **2017**, *173*, 551–556. [[CrossRef](#)] [[PubMed](#)]
24. Agrafioti, E.; Bouras, G.; Kalderis, D.; Diamadopoulou, E. Biochar production by sewage sludge pyrolysis. *J. Anal. Appl. Pyrolysis* **2013**, *101*, 72–78. [[CrossRef](#)]
25. Lu, H.L.; Zhang, W.H.; Wang, S.Z.; Zhuang, L.W.; Yang, Y.X.; Qiu, R.L. Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. *J. Anal. Appl. Pyrolysis* **2013**, *102*, 137–143. [[CrossRef](#)]
26. GB15618. *Environmental Quality Standard for Soils*; State Environmental Protection Administration, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, China Standards Press: Beijing, China, 1995; pp. 1–3.
27. GB/T 212–2008. *Proximate Analysis of Coal*; Standardization administration of the People's Republic of China, State Environmental Protection Administration, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China: Beijing, China, 2008; pp. 3–5.
28. Lu, R.K. *Soil and Agro-Chemical Analytical Methods*; China Agricultural Science and Technology Press: Beijing, China, 1999. (In Chinese)

29. Koschke, L.; Lorz, C.; Fürst, C.; Glaser, B.; Makeschin, F. Black carbon in fly-ash influenced soils of the Dübener Heide region, central Germany. *Water Air Soil Pollut.* **2011**, *214*, 119–132. [[CrossRef](#)]
30. Zhang, G.; Zhao, Y.; Yang, J.; Zhao, W.; Gong, Z. Urban soil environment issues and research progress (Chinese with English abstract). *Acta Pedol. Sin.* **2007**, *44*, 925–933.
31. Joseph, S.; Kammann, C.I.; Shepherd, J.G.; Conte, P.; Schmidt, H.P.; Hagemann, N.; Rich, A.M.; Marjo, C.; Allen, J.A.; Munroe, P.; et al. Microstructural and associated chemical changes during the composting of a high temperature biochar: Mechanisms for nitrate, phosphate and other nutrient retention and release. *Sci. Total Environ.* **2018**, *618*, 1210–1223. [[CrossRef](#)] [[PubMed](#)]
32. Hossain, M.K.; Strezov, V.; Chan, K.Y.; Ziolkowski, A.; Nelson, P.F. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *J. Environ. Manag.* **2011**, *92*, 223–228. [[CrossRef](#)] [[PubMed](#)]
33. Bird, M.I.; Mcbeath, A.V.; Ascough, P.L.; Levchenko, V.A.; Wurster, C.M.; Munksgaard, N.C.; Smernik, R.J.; Williams, A. Loss and gain of carbon during char degradation. *Soil Biol. Biochem.* **2017**, *106*, 80–89. [[CrossRef](#)]
34. Zimmermann, M.; Bird, M.I.; Wurster, C.; Saiz, G.; Goodrick, I.; Barta, J.; Capek, P.; Santruckova, H.; Smernik, R. Rapid degradation of pyrogenic carbon. *Glob. Chang. Biol.* **2012**, *18*, 3306–3316. [[CrossRef](#)]
35. Kim, Y.; Parker, W. A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. *Bioresour. Technol.* **2008**, *99*, 1409–1416. [[CrossRef](#)]
36. Gaskin, J.W.; Speir, A.; Morris, L.M.; Ogden, L.; Harris, K.; Lee, D.; Das, K.C. Potential for pyrolysis char to affect soil moisture and nutrient status of a loamy sand soil. In Proceedings of the 2007 Georgia Water Resources Conference, Georgia, Athens, 27–29 March 2007; pp. 27–29.
37. Xu, X.; Zhao, Y.H.; Sima, J.; Zhao, L.; Mašek, O.; Cao, X.D. Indispensable role of biochar-inherent mineral constituents in its environmental applications: A review. *Bioresour. Technol.* **2017**, *241*, 887–899. [[CrossRef](#)] [[PubMed](#)]
38. Omondi, M.O.; Xia, X.; Nahayo, A.; Liu, X.; Korai, P.K.; Pan, G.X. Quantification of biochar effects on soil hydrological properties using meta-analysis of literature data. *Geoderma* **2016**, *274*, 28–34. [[CrossRef](#)]
39. Petersen, C.T.; Hansen, E.; Larsen, H.H.; Hansen, L.V.; Ahrenfeldt, J.; Hauggaard-Nielsen, H. Pore-size distribution and compressibility of coarse sandy subsoil with added biochar. *Eur. J. Soil Sci.* **2016**, *67*, 726–736. [[CrossRef](#)]
40. Kidd, P.S.; Domínguez-Rodríguez, M.J.; Diez, J.; Monterroso, C. Bioavailability and plant accumulation of heavy metals and phosphorus in agricultural soils amended by long-term application of sewage sludge. *Chemosphere* **2007**, *66*, 1458–1467. [[CrossRef](#)]
41. Jin, J.J.; Li, Y.N.; Zhang, J.Y.; Wu, S.C.; Cao, Y.C.; Liang, P.; Zhang, J.; Wong, M.H.; Wang, M.Y.; Shan, S.D.; et al. Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge. *J. Hazard. Mater.* **2016**, *320*, 417–426. [[CrossRef](#)] [[PubMed](#)]
42. Chen, Y.W.; Liu, G.J.; Lei, W.; Yu, K.; Yang, J. Occurrence and fate of some trace elements during pyrolysis of Yima coal, China. *Energy Fuel* **2008**, *22*, 3877–3882.
43. Song, X.D.; Xue, X.Y.; Chen, D.Z.; He, P.J.; Dai, X.H. Application of biochar from sewage sludge to plant cultivation: Influence of pyrolysis temperature and biochar-to-soil ratio on yield and heavy metal accumulation. *Chemosphere* **2014**, *109*, 213–220. [[CrossRef](#)]
44. Beesley, L.; Inneh, O.S.; Norton, G.J.; Moreno-Jimenez, E.; Pardo, T.; Clemente, R.; Dawson, J.J.C. Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. *Environ. Pollut.* **2014**, *186*, 195–202. [[CrossRef](#)] [[PubMed](#)]
45. Mohamed, I.; Zhang, G.S.; Li, Z.G.; Liu, Y.; Chen, F.; Dai, K. Ecological restoration of an acidic Cd contaminated soil using bamboo biochar application. *Ecol. Eng.* **2015**, *84*, 67–76. [[CrossRef](#)]
46. Choppala, G.; Bolan, N.; Kunhikrishnan, A.; Bush, R. Differential effect of biochar upon reduction-induced mobility and bioavailability of arsenate and chromate. *Chemosphere* **2016**, *144*, 374–381. [[CrossRef](#)] [[PubMed](#)]
47. Dong, X.L.; Ma, L.Q.; Li, Y.C. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *J. Hazard. Mater.* **2011**, *190*, 909–915. [[CrossRef](#)]
48. Harvey, O.R.; Herbert, B.E.; Rhue, R.D.; Kuo, L.J. Metal interactions at the biochar-water interface: Energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. *Environ. Sci. Technol.* **2011**, *45*, 5550–5556. [[CrossRef](#)] [[PubMed](#)]
49. Chen, X.J.; Lin, Q.M.; He, R.D.; Zhao, X.R.; Li, G.T. Hydrochar production from watermelon peel by hydrothermal carbonization. *Bioresour. Technol.* **2017**, *241*, 236–243. [[CrossRef](#)]

50. Puga, A.P.; Abreu, C.A.; Melo, L.C.A.; Beesley, L. Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. *J. Environ. Sci.* **2015**, *159*, 86–93. [[CrossRef](#)]
51. Fang, S.E.; Tsang, D.C.W.; Zhou, F.S.; Zhang, W.H.; Qiu, R.L. Stabilization of cationic and anionic metal species in contaminated soils using sludge-derived biochar. *Chemosphere* **2016**, *149*, 263–271. [[CrossRef](#)]
52. Akhtar, S.S.; Li, G.T.; Andersen, M.N.; Liu, F.L. Biochar enhances yield and quality of tomato under reduced irrigation. *Agric. Water Manag.* **2014**, *138*, 37–44. [[CrossRef](#)]
53. Hossain, M.K.; Strezov, V.; Nelson, P.F. Comparative assessment of the effect of wastewater sludge biochar on growth, yield and metal bioaccumulation of cherry tomato. *Pedosphere* **2015**, *25*, 680–685. [[CrossRef](#)]
54. Wang, Q.; Chen, L.; He, L.Y.; Sheng, X.F. Increased biomass and reduced heavy metal accumulation of edible tissues of vegetable crops in the presence of plant growth-promoting *neorhizobium huautlense* T1-17 and biochar. *Agric. Ecosyst. Environ.* **2016**, *228*, 9–18. [[CrossRef](#)]
55. Ran, J.; Wang, D.J.; Wang, C.; Zhang, G.; Zhang, H.L. Heavy metal contents, distribution, and prediction in a regional soil-wheat system. *Sci. Total Environ.* **2016**, *544*, 422–431. [[CrossRef](#)] [[PubMed](#)]
56. Zeng, F.R.; Ali, S.; Zhang, H.T.; Ouyang, Y.N.; Qiu, B.Y.; Wu, F.B.; Zhang, G.P. The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environ. Pollut.* **2011**, *159*, 84–91. [[CrossRef](#)] [[PubMed](#)]
57. Yin, Y.; Allen, H.E.; Li, Y.; Huang, C.P.; Sanders, P.F. Adsorption of mercury (II) by soil: Effects of pH, chloride, and organic matter. *J. Environ. Qual.* **1996**, *25*, 837–844. [[CrossRef](#)]
58. Xu, P.; Sun, C.X.; Ye, X.Z.; Xiao, W.D.; Zhang, Q.; Wang, Q. The effect of biochar and crop straws on heavy metal bioavailability and plant accumulation in a Cd and Pb polluted soil. *Ecotoxicol. Environ. Saf.* **2016**, *132*, 94–100. [[CrossRef](#)] [[PubMed](#)]
59. Lu, K.P.; Yang, X.; Gielen, G.; Bolan, N.; Ok, Y.S.; Niazi, N.K.; Xu, S.; Yuan, G.D.; Chen, X.; Zhang, X.K.; et al. Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. *J. Environ. Manag.* **2017**, *186*, 285–292. [[CrossRef](#)] [[PubMed](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).