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Barley Straw Biochar and Compost Affect Heavy Metal Transport in Soil and Uptake by Potatoes Grown under Wastewater Irrigation

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Abstract: Wastewater can supplement freshwater in agriculture; however, it contains toxic heavy metals such as cadmium, chromium, and lead that are hazardous to humans and the environment. We investigated the effects of barley straw biochar, green and table waste compost, and their mix on heavy metal transport in soil and uptake by potatoes (*Solanum tuberosum* L.) irrigated with synthetic wastewater for two years. In both years, amending soil with compost significantly reduced ($p \leq 0.05$) cadmium uptake in potato flesh, skin, roots, and stems; zinc uptake in potato skin and roots; and copper uptake in potato flesh due to increased soil cation-exchange capacity, dissolved organic carbon, and soil pH. Co-amending the soil with compost and 3% biochar significantly reduced ($p \leq 0.05$) the bioavailability of cadmium, copper, and zinc in the contaminated soil. Relative to the non-amended soils, soil amendment with biochar, compost, and their mix affected neither the transport of chromium, iron, and lead in the soils nor their uptake by potatoes. It was concluded that amending soil with barley straw biochar and/or compost produced from city green table waste could be used to improve the safety of wastewater irrigated potatoes, depending on the biochar application rate and heavy metal type.

Keywords: heavy metals; soil amendments; plant uptake; potatoes; sandy soil; wastewater irrigation

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1. Introduction

Wastewater can supplement freshwater demand for irrigation, reduce stress on freshwater resources, and ease the problem of wastewater disposal [1,2]. However, wastewater contains toxic heavy metals such as arsenic (As), lead (Pb), mercury (Hg), and cadmium (Cd) [3], which are hazardous substances that are ranked first through fourth, respectively, according to the US Agency for Toxic Substances and Disease Registry [4]. When added to soils through wastewater irrigation, heavy metals are likely to be a greater cause for concern because they can translocate to plants and reach the human food chain.

The uptake of heavy metals by plants has been widely studied [5–7]. Plants can uptake soluble forms of heavy metals within the root zone and can easily solubilize particle-bound heavy metals with root exudates [8,9]. Plants are capable of accumulating both essential and non-essential heavy metals [10]. Biologically essential heavy metals (oligoelements) include copper (Cu), iron (Fe), nickel (Ni), and zinc (Zn), while non-essential heavy metals include As, Cd, chromium (Cr), Hg, Pb, and tin (Sn). Because heavy metals, especially non-essential metals, are harmful through all trophic levels, techniques to reduce their mobility and bioavailability in soil and translocation to plants are urgently needed to ensure the safe use of wastewater.

Soil amendments such as biochars have been proposed to reduce the risks associated with using wastewater in agriculture. Biochar is a carbon-rich end-product of biomass pyrolysis with a high capacity to adsorb heavy metals due to its high surface area and abundance of surface functional groups [11]. Biochar is typically alkaline, which helps raise soil pH and stabilize heavy metals, thus reducing their leaching and uptake by crops [12]. Laboratory and field-scale experiments have shown that biochar amendments have the potential to reduce the movement of inorganic contaminants (such as heavy metals) in soil and water systems, as well as to reduce their uptake by plants [13–15].

Compost, another soil amendment, is a stable, humus-like substance, produced through the thermophilic biodegradation of organic materials; it is different from biochar in properties and functions, and it can be used to improve soil structure and increase soil organic matter (SOM) and cation-exchange capacity (CEC), thereby improving soil fertility and metal mobility [16]. Kocasoy and Güvener [17] determined the retention capacity of compost for several heavy metals (Cu, Zn, Ni, and Cr). The authors concluded that compost has high retention capacities for Cu, Zn, and Ni but not for Cr at concentrations ranging from 100 to 1000 mg L^{-1}. The greater CEC conferred by compost has been shown to reduce heavy metal bioavailability in the soil through co-precipitation and immobilization through sorption [18,19].

Despite research proving the viability of biochar and compost for the remediation of heavy metals, few studies have examined the impact of different rates of biochar application [20–23] or mixed biochar–compost soil amendments [24–27]. Mixing biochar and compost could be an innovative technique to increase fertility in contaminated soils, with the performance of such a mixture depending on feedstock type. Although barley straw biochar has shown potential for removing Pb and Cd from aqueous solutions [28], its effectiveness of amending alone or in combination with green and kitchen waste compost at different rates on the transport of heavy metals, such as Cd, Cr, Cu, Fe, Pb, and Zn in sandy soil and/or translocation to crops—especially belowground crops, such as potatoes, which are prone to contamination through direct contact with wastewater—has not been explored. Therefore, we conducted a two-year study to evaluate the effects of two biochar application rates (1% and 3% *w*/*w*), alone or in combination with compost (7.5% *w*/*w*), on the fate of wastewater-borne heavy metals in a sandy soil and their uptake by a potato (*Solanum tuberosum* L.) crop irrigated with wastewater containing heavy metals.

2. Materials and Methods

2.1. Experimental Setup

The field study was conducted in lysimeters located at the Macdonald Campus of McGill University, Sainte-Anne-de-Bellevue QC, Canada (lat. 45°24′48.6″ N, long. 73°56′28.1″ W). Polyvinyl chloride lysimeters (height of 1 m in and inner diameter of 0.45 m), sealed at the bottom with a polyvinyl chloride sheet and provided with a perforated drainage pipe, were filled with a sandy soil obtained from the farm of the Macdonald Campus of McGill University. The properties of the soil prior to its mixing with amendments and wastewater irrigation are given in Table 1 [29].

Six treatments, in triplicate, were randomly allocated to 18 lysimeters. The treatments were: (i) wastewater control, BC_0CP_0; (ii) 1% biochar and no compost, BC_1CP_0; (iii) 3% biochar and no compost, BC_3CP_0; (iv) no biochar and 7.5% compost, $BC_0CP_{7.5}$; (v) 1% biochar and 7.5% compost, $BC_1CP_{7.5}$; and (vi) 3% biochar and 7.5% compost, $BC_3CP_{7.5}$. Prior to the imposition of treatments, soil samples were taken from surface soil at depths of 0.10 and 0.30 m to determine important soil properties affecting heavy metals' fate and transport in soil and their uptake by plants, i.e., CEC, DOC, and pH. Compost and biochar were also analyzed for heavy metals and nutrients. In the first year, appropriate quantities of biochar and compost (*w*/*w*) were thoroughly mixed in the upper 0.1 m of soil in the lysimeters. For two weeks prior to planting, potato seed tubers (cv. 'Russet Burbank') were stored at 8–10 °C in a cardboard box covered with cheesecloth to encourage budding. One potato tuber was planted in each lysimeter, with the most prominent bud facing upwards. In both years, three fertilizers, i.e., urea, triple superphosphate, and potassium chloride, were applied in a ring around the tuber according to the local recommendation rates for potato (cv. Russet Burbank): N was applied at the rate of 180 kg N ha^{-1} [30]; 30% of N fertilizer was applied on day 0, 30% was applied on day 31 after planting, and the remaining 40% was applied in four equal parts on days 46, 53, 60, and 67 post-planting [31]. Each season, at planting, all treatments received 280 kg K ha^{-1} and 44 kg P ha^{-1} [30] on day 0. A canvas tent was setup over the lysimeters to prevent natural precipitation from entering them. Each lysimeter manually received 11.5 L of wastewater every 10 days. A total of eight irrigations were applied per season. The concentrations of various contaminants in the synthetic wastewater are given in Table 2 [29]. The concentrations of contaminants were determined based on worst-case scenarios from the global literature on wastewater contamination.

Table 1. Soil physiochemical properties prior to soil amendments.

Mineral Components	Values (mg kg^{-1})	Soil Properties	Values
N	3.67 ± 0.21	Sand (%)	92.2
P	74.7 ± 3.52	Silt (%)	4.3
K	54.7 ± 6.03	Clay (%)	3.5
Mg	50.0 ± 2.93	pH	5.61 ± 0.19
Ca	754 ± 48.15	SOM (%)	1.82 ± 0.05
Al	1689.2 ± 96.85	EC (mS cm^{-1})	66.43 ± 11.13
Mn	1.9 ± 0.22	ZPC	3.40
Cd	<LOD	CEC (cmol(+) kg^{-1})	3.35 ± 0.33
Cr	21.1 ± 2.81	C (%)	0.82 ± 0.14
Cu	6.8 ± 1.24	N (%)	0.085
Fe	8822 ± 352.14	C: N Ratio	9.61 ± 0.72
Pb	<LOD	DOC (mg kg^{-1})	29.52 ± 2.15
Zn	22 ± 5.14	Bulk Density (Mg m^{-3})	1.35

SOM: soil organic matter; EC: electrical conductivity; ZPC: zero point of charge; CEC: cation-exchange capacity; DOC: dissolved organic carbon; LOD: limit of detection; N, P, K, Mg, Ca, Mn, and Al were determined using Mehlich III extraction [32]; the heavy metals Cd, Cr, Cu, Fe, Pb, and Zn were determined using hot acid extraction [25] and quantified with ICP-OES. Other soil properties were adapted from a previous study conducted with soil from the same field [33].

Potatoes were harvested 120 days after planting, and their aboveground biomass was separated into stems and leaves. Underground biomass was separated into roots and tubers. Potato tubers were peeled to separate flesh and skin. The aboveground biomass (stems and leaves) and underground biomass (roots, skin, and flesh of tuber) were washed with deionized water and air-dried. Tuber flesh was longitudinally dissected and further diced into about 10 mm cubes, washed, and oven dried at 60 °C for 48 h. Dried samples were then ground for heavy metal analysis. Soil samples from each lysimeter were collected at the end of each season (2017 and 2018). Soil cores of the top 0.10 m soil layer were sampled at 20-mm intervals, as well as at the 30 cm depth after harvesting. After the completion of the first year of the experiment, the tent was removed and the lysimeters were covered with plastic bags to prevent water from rainfall or snow entering them over the winter months. In the second year, the tent was again set up, but amendments were not applied and the same lysimeters were used for respective treatments. At the end of the second season, potatoes were harvested and soil samples were collected for heavy metal analysis. Soil samples were also taken from the surface soil and at the 0.10-m depth to determine CEC, DOC, and pH.

Table 2. Components and concentrations (mg L^{-1}) in synthetic wastewater.

Category	Substance/Compounds	Country	Concentration	Reference
Basic synthetic wastewater constituents				
C Source	Na Acetate	NA	79.37	[34]
	Milk powder	NA	116.19	
	Soy Oil	NA	29.02	
	Starch	NA	122	
	Yeast Extract	NA	52.24	
N Source	NH_4Cl	NA	12.75	
	Peptone	NA	17.41	
	Urea	NA	91.74	
P Source	$Mg_3O_8P_2$	NA	29.02	
Minerals	$CaCl_2$	NA	60	[35]
	$NaHCO_3$	NA	100	
Surfactant	Triton X-100	NA	* 30	[36]
Wastewater contaminants				
Heavy Metals	Chromium (Cr)	India	2	[37]
	Cadmium (Cd)	India	5	
	Lead (Pb)	India	16	
	Iron (Fe)(II)	India	120	
	Zinc (Zn)	India	3	
	Copper (Cu)(II)	India	8	
Hormones	Estrone: E1	S. Korea	* 8.15 (20)	[38]
	Estradiol: E2	S. Korea	* 0.634 (20)	
	Estriol: E3	S. Korea	* 2.28 (20)	
	Ethinylestradiol: EE2	China	* 0.33 (20)	[39]
	Progesterone	China	* 0.90 (20)	[40]
PPCPs	Ibuprofen	Canada	* 45	[41]
	DEET	USA	* 6.5	[42]
	Caffeine	China	* 6.6	[43]
	Carbamazepine	S. Korea	* 21.6	[38]
	Diclofenac	India	* 25.68	[44]
	Triclosan	UK	* 21.9	[45]
	Oxytetracycline	China	* 19.5	[46]

* Concentrations in μg L^{-1}; NA: not applicable; PPCPs: pharmaceutical and personal care products; numbers in () indicates the concentration used in this work.

2.2. Physicochemical Characterization of Biochar and Compost

Barley straw biochar was purchased from InnoTech Alberta (Canada). Prior to carbonization, barley straw was chopped into pieces less than 50 mm long. Pyrolysis was then performed in a Batch Rotary Drum (80″ length × 24″ diameter) at ~535 °C for 28 min (total retention time: 83 min). The final product was cooled under CO2 gas purging for 2–3 h. The compost was derived from mixed green and table waste from the city of Baie-D'Urfé in the West Island region of the island of Montreal (QC, Canada).

Barley straw biochar and compost samples were subjected to an ultimate and proximate analysis at the CanmetENERGY (NRC) Characterization Laboratory, Ottawa, ON, Canada. The moisture content, ash content, volatile matter content, and fixed carbon content (ASTM D7582 and ISO 562 for volatiles) were determined with proximate analysis. Levels of C, H, O, N, and S were determined through ultimate analysis (ASTM D5373 and ASTM D4239 for S). The heavy metal content was determined in the Bioresource Engineering Department (BED) Laboratory of McGill University following hot acid extraction [25,47]. The P, K, Calcium (Ca), Magnesium (Mg), and Manganese (Mn) levels were determined using Mehlich III extraction [32], while N was determined according to the methods of Carter and Gregorich [48]. The results of the analyses are shown in Table A1.

2.3. Sample Extraction and Quantification

Soil analysis was undertaken in the BED Laboratory. Soil DOC was determined using a TOC analyzer (Sievers InnovOx Laboratory). CEC was measured using the $BaCl_2$ method by Hendershot et al. [49], while pH was measured using a pH electrode (Accumet pH meter model AB15, Fisher Scientific, Waltham, MA, USA) following the method of Rayment and Higginson [50].

The hot nitric acid digestion method [25,47] was used to determine the heavy metal concentrations in soil samples and plant tissues. A homogenized sample of 0.16 g was added to a 15 mL test tube with 2 mL of concentrated nitric acid (trace metal grade: 70% pure). The solution was allowed to equilibrate overnight. Samples were then placed on a block digester (Fisher Scientific®, dry batch incubator), where the temperature was gradually increased to 80 °C and then maintained until any brown color disappeared. The temperature was further gradually increased to 120 ± 5 °C and maintained at this temperature for 5 h. Samples were removed and cooled for 15 min. The digested solution was transferred to 50 mL Falcon tubes and diluted to 50 mL with deionized water before being stored at 4 °C until heavy metal quantification. The soil samples were analyzed with an inductively coupled plasma optical emission spectrometry equipment (ICP-OES, Varian, Vista-MPX CCD, Varian Inc., Mulgrave, Victoria, Australia). Plant tissue samples were analyzed with an inductively coupled plasma mass spectrometry (ICP-MS, Varian ICP820-MS, Varian Inc., Victoria, Australia). To ensure quality control, reference materials (SED98-04 and SED92-03, Environment Canada) and blanks were added to all runs.

2.4. Statistical Analysis

Heavy metal concentration in soil was assigned as a response variable, and treatment and depth were assigned as fixed-effect variables. The data were analyzed using the GLM procedure of SAS 9.4 (SAS Institute Inc., Cary, NC, USA). A chi-squared test was used to confirm normality, and Levene's test was used to confirm the homogeneity of variance. The concentrations of heavy metals in the plant tissues data and soil physicochemical properties were analyzed using a one-way analysis of variance (ANOVA), considering treatment as the only factor; differences were considered significant when $p \leq 0.05$. When the ANOVA results showed a significant difference, the least significant difference (LSD) post hoc test was applied.

3. Results

3.1. Effects of Soil Amendment on Soil Properties

The soil CEC, DOC, and pH in the different treatments at the surface and 0.10 m soil depth are presented in Table 3. The bulk soil CEC, before the experiment, was 3 cmol kg^{-1}; see Table 1. The CEC decreased to 1.78 and 2.62 cmol kg^{-1} in BC_0CP_0 (no soil amendment) at both the 0 and 0.10 m depths after two years of wastewater irrigation. Treatments receiving compost ($BC_3CP_{7.5}$, $BC_1CP_{7.5}$, and $BC_0CP_{7.5}$) had greater ($p \leq 0.05$) CEC values at the surface and 0.1 m depth than their respective non-compost-receiving treatments (BC_0CP_0, BC_1CP_0, and BC_3CP_0). This indicated that irrespective of biochar application rate, the addition of compost increased the CEC. It was also observed that at the soil surface, the CEC for each compost treatment exceeded that of all treatments without compost. At 0.10 m, only BC_0CP_0, and BC_1CP_0 differed from the $CP_{7.5}$ treatments, and only $BC_3CP_{7.5}$ differed from the CP_0 treatments. This indicated that the addition of 3% biochar likely increased the CEC. No significant differences in the soil CEC were found between the BC_0CP_0, BC_1CP_0, and BC_3CP_0 treatments at the soil's surface or the 0.10 m depth.

Table 3. CEC, DOC, and pH at the surface and 0.1 m depth in different treatments at the end of two years.

Treatments	CEC (cmolc kg^{-1})		DOC (mg kg^{-1})		pH	
	Surface	0.10 m	Surface	0.10 m	Surface	0.10 cm
BC_0CP_0	1.78 ± 0.29 b	2.62 ± 1.24 c	13.17 ± 0.85 d	12.61 ± 0.75 b	5.00 ± 0.10 d	5.26 ± 0.14 d
BC_1CP_0	1.69 ± 0.31 b	1.88 ± 0.33 c	11.62 ± 1.18 d	11.68 ± 3.27 b	5.18 ± 0.15 cd	5 ± 0.2 d
BC_3CP_0	1.94 ± 0.44 b	4.12 ± 1.34 bc	13.38 ± 1.67 d	19.85 ± 0.20 ab	5.33 ± 0.14 bc	6.11 ± 0.03 c
$BC_0CP_{7.5}$	4.58 ± 0.94 a	7.39 ± 0.93 ab	27.31 ± 1.06 a	24.10 ± 11.36 a	5.60 ± 0.10 a	6.43 ± 0.3 bc
$BC_1CP_{7.5}$	4.60 ± 1.46 a	5.54 ± 0.29 b	23.35 ± 2.69 b	24.90 ± 2.45 a	5.43 ± 0.17 ab	6.5 ± 0.14 b
$BC_3CP_{7.5}$	5.73 ± 2.74 a	7.57 ± 1.60 a	18.33 ± 1.75 c	28.43 ± 8.03 a	5.66 ± 0.11 a	7.13 ± 0.15 a

The different letters in each column represent a significant difference at $p \leq 0.05$; values are mean $\pm$ standard error of three replicates. BC_0CP_0: non-amended soil; BC_1CP_0: 1% biochar alone; BC_3CP_0: 3% biochar alone; $BC_0CP_{7.5}$: 7.5% compost alone; $BC_1CP_{7.5}$: 1% biochar and 7.5% compost; and $BC_3CP_{7.5}$: 3% biochar and 7.5% compost.

The DOC of the soil before the experiment was 29.5 mg kg^{-1}; see Table 1. After two years, it was lower than the background value. This could have been due to the leaching of DOC to lower depths in this sandy soil. It decreased to 12.89 mg kg^{-1} (average of surface and 0.1 m) in BC_0CP_0 under wastewater irrigation. The DOC at the soil surface was significantly higher ($p \leq 0.05$) in the $BC_0CP_{7.5}$ treatment compared to other treatments, followed by $BC_1CP_{7.5}$ and then $BC_3CP_{7.5}$; see Table 3. The biochar-alone treatments (BC_1CP_0 and BC_3CP_0) produced no significant difference ($p > 0.05$) in DOC compared to the non-amended BC_0CP_0 (control). At the 0.10 m depth, compost amendment alone or in combination with biochar led to significantly greater ($p \leq 0.05$) DOC concentrations than the BC_0CP_0 and BC_1CP_0 treatments. The DOC under BC_3CP_0 was moderate and not significantly different than any other treatment. The results indicated that the increased DOC in soil was mainly due to compost. The trends in the DOC were similar to those of the CEC, with amendment with 3% (vs. 1%) biochar leading to greater CEC values.

The initial pH of the sandy soil was 5.5; see Table 1. After wastewater irrigation, the soil pH without amendment (BC_0CP_0 and BC_1CP_0) was slightly lower than 5.5 in both depths; see Table 3. At the surface or the 0.10 m depth, the soil treatments of $BC_0CP_{7.5}$ and $BC_3CP_{7.5}$ had a greater ($p \leq 0.05$) soil pH than that of the BC_0CP_0 and BC_1CP_0 amendments; no significant differences were observed in the pH between BC_0CP_0 and BC_1CP_0. Soil amendment with 3% biochar clearly increased the soil pH at the 0.10 m depth. The pH was also significantly increased by compost amendment; $BC_3CP_{7.5}$ showed a greater ($p \leq 0.05$) pH value than that of BC_3CP_0 at both depths, indicating that compost had the greatest impact on pH. Similarly, $BC_1CP_{7.5}$ showed a greater ($p \leq 0.05$) pH than BC_1CP_0 at both depths. Overall, pH was significantly higher in the compost treatments compared to those without compost, irrespective of biochar content.

Overall, the 7.5% compost amendment significantly increased the CEC, DOC, and pH. Although the 1% biochar amendment had minimal impact on these parameters, the 3% biochar amendment caused a slight increase in these soil properties. Considering the average between the surface and 0.1 m depth values, it was observed that there were increases in the CEC, DOC, and pH by about 0.83 cmol kg^{-1}, 3.725 mg kg^{-1}, and 0.59, respectively, compared to the non-amended treatment due to the 3% biochar amendment. On the other hand, the corresponding increases were 3.785 cmol kg^{-1}, 12.815 mg kg^{-1}, and 0.885 for 7.5% compost alone. These values indicate that the amendment of 7.5% compost was more effective in increasing these parameters than 3% biochar. With the amendment of both 3% biochar and 7.5% compost, the differences further increased to 4.45 cmol, 10.49 mg kg^{-1}, and 1.765, respectively. These results indicate that although 7.5% compost was quite effective, 3% biochar applied in combination was also effective.

3.2. Effect of Soil Amendments on Heavy Metals Mobility in Soil

The soil amendments also impacted heavy metal mobility in the soil. The initial concentrations of toxic (Cd, Cr, and Pb) and non-toxic metals (Cu, Fe, and Zn) in the soil are given in Table 1. Figure 1 and Tables A2–A4 show heavy metal concentrations at the end of both experiments in 2017 and 2018 at the 0–20, 20–40, 40–60, 60–80, and 80–100 mm depth ranges. In addition, Table A5 shows the heavy metal concentrations at the 30 cm depth.

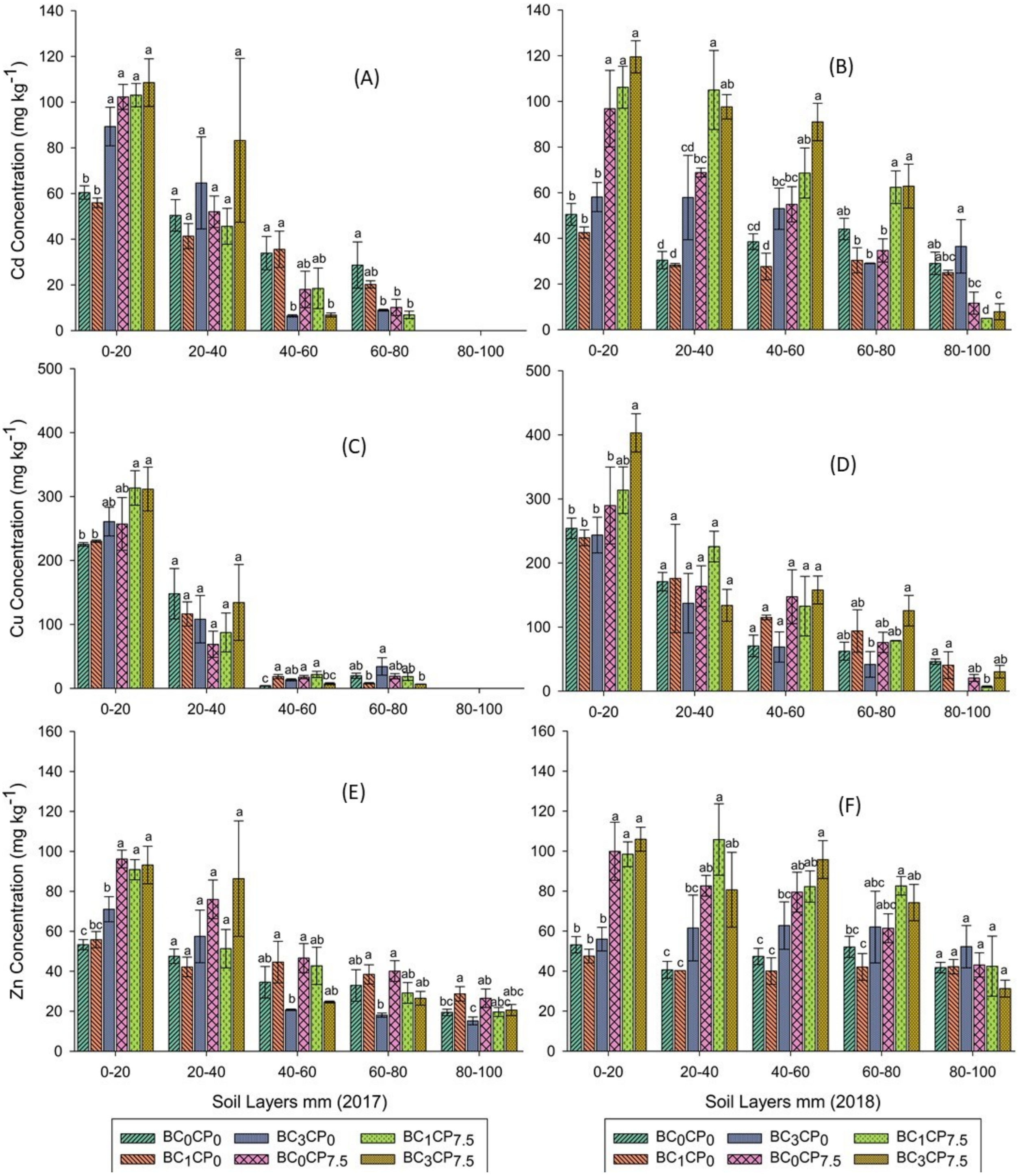

Figure 1. Effect of biochar and/or compost amendments on (**A**,**B**) Cd, (**C**,**D**) Cu, and (**E**,**F**) Zn concentration (mg kg^{-1}) in different soil layers on the day of harvest in 2017 (**A**,**C**,**E**) and in 2018 (**B**,**D**,**F**). The different letters above bars in a given column represent significant difference at $p \leq 0.05$. Error bars are standard error of three replicates. BC_0CP_0: non-amended soil; BC_1CP_0: 1% biochar alone; BC_3CP_0: 3% biochar alone; $BC_0CP_{7.5}$: 7.5% compost alone; $BC_1CP_{7.5}$: 1% biochar and 7.5% compost; and $BC_3CP_{7.5}$: 3% biochar and 7.5% compost.

The initial soil Cd concentration was below detection limits; see Table 1. After wastewater irrigation, soil Cd in 2017 was detected at depths of up to 60 mm in $BC_3CP_{7.5}$ plots and of up to 80 mm in all remaining treatments; see Figure 1A,B. Soil Cd was greatest in the 0–20 mm layer and gradually decreased with depth in all treatments, indicating that Cd slowly leached downward due to irrigation. In the top layer (0–20 mm), the soil Cd was significantly greater ($p \leq 0.05$) for compost treatments, with or without biochar, and greater for BC_3CP_0 soil than the non-amended (BC_0CP_0) or BC_1CP_0 soils. This could have been because the CEC in compost-amended treatments was significantly greater ($p \leq 0.05$) than that in treatments with no-compost. The higher biochar content (3%) also had an impact; the CEC for the BC_3CP_0 treatment was greater than that of BC_0CP_0 or BC_1CP_0. Cd in irrigation wastewater can be better adsorbed in soil with a greater CEC. While the soil Cd concentration at 20–40 mm was similar across all treatments, it was significantly greater ($p \leq 0.05$) at lower soil depths in BC_0CP_0 and BC_1CP_0 than under the other treatments. These results indicate that 3% biochar and compost reduced the mobility of Cd.

In year two (2018), soil Cd was also detected in the 80–100 mm soil layer, indicating that soil Cd continued to move downward with the continued application of wastewater. Again, the soil Cd concentration was lower nearer to the surface (0–20, 20–40, and 40–60 mm) and higher at 80–100 mm in the BC_0CP_0 and BC_1CP_0 treatments than under the remaining treatments. This confirms that compost and 3% biochar reduced Cd mobility at the soil surface and in lower soil layers. A larger proportion of soil Cd was adsorbed near the soil surface in the treatments with 3% biochar and/or compost.

While the treatments had a significant influence on soil Cd concentrations, results were inconclusive for Cr and Pb. The concentration of Cr in the soil at the end of the experiment in both years is given in Table A2. The initial concentration of Cr in soil was 21 mg kg^{-1}. In 2017, there was no effect of amendments on the soil Cr concentration across all depths. Cr concentrations were noticeably higher in treatments with compost, although no statistically significant differences were observed. The same trend was observed in 2018 at the 40–60 and 80–100 mm layers; however, there was no conclusive evidence that the compost amendment led to the greater adsorption of soil Cr. Overall and as expected, the concentration in 2018 was higher than in 2017 due to the continued application of wastewater irrigation.

Lead was not detected in the soil before the experiment; see Table 1. In 2017, all treatments showed detectable Pb in all soil layers except for 80–100 mm, but no significant differences among the treatments were observed; see Table A3. Generally, soil Pb concentration decreased as depth increased, suggesting that Pb moved slowly in soil with the application of wastewater. After continued wastewater irrigation in 2018, Pb was detected in the 80–100 mm soil layer and concentrations decreased with depth. Generally, the soil Pb concentrations were significantly higher ($p \leq 0.05$) in 2018 than in 2017 due to the continuation of wastewater irrigation.

Regarding the non-toxic metals, biochar and compost also had no impact on Fe mobility. The initial soil Fe concentration was 8822 mg kg^{-1}; see Table 1. The Fe soil concentrations increased due to wastewater irrigation, but there was no significant difference between treatments; see Table A4. In both years, the concentration gradually decreased with depth in all treatments. In 2017, the average concentration was 15,724 mg kg^{-1} at 0–20 mm, which decreased to 12,787 mg kg^{-1} at the 80–100 mm depth. In 2018, the corresponding concentrations were 16,122 (0–20 mm) and 12,832 (80–100 mm) mg kg^{-1}, indicating that Fe readily moved from the surface to lower depths in the soil, even beyond 100 mm.

Conversely, the treatments did impact the mobility of Cu and Zn. In 2017, the soil Cu concentration at 0–20 mm was greater ($p \leq 0.05$) in the $BC_1CP_{7.5}$ and $BC_3CP_{7.5}$ treatments than in other treatments (Figure 1C,D), suggesting that compost, with or without biochar, significantly increased soil Cu adsorption. Similarly to Cd, when biochar was applied alone, the 3% biochar amendment provided a greater adsorption of Cu than 1% biochar. The concentration gradually decreased with depth in all treatments. There was no significant effect of amendments on Cu in the 20–40 mm soil depth. Differences in concentration among treatments in the 40–60 and 60–80-mm depths were observed, but the concentrations were relatively low. Cu was not detected at 80–100 mm in 2017.

In 2018, Cu was detected at 80–100 mm, and concentrations declined with depth. At the surface soil, the Cu concentration in mixed biochar- and compost-amended plots ($BC_1CP_{7.5}$ and $BC_3CP_{7.5}$) was significantly higher than in other treatments. Irrespective of treatments, concentrations of Cu were slightly greater in 2018 than in 2017; the mean Cu concentrations across all treatments were 9, 52, 745, and 353% higher in 2018 for the 0–20, 20–40, 40–60, and 60–80 mm depths, respectively. Given that differences in the surface layers were quite low but substantially larger at the 40–80 mm depth, it appears that adsorption sites in the upper layers were quickly saturated and could therefore no longer hold additional Cu. It also appears that 1% biochar alone was ineffective in preventing Cu transport, but the biochar compost mix could bind Cu added through irrigation water.

The compost amendment increased Zn concentration ($p \leq 0.05$) in the 0–20 mm soil layer compared to treatments not receiving any compost; see Figure 1E,F. At other depths, no clear trend was observed. In 2018, the effect of compost amendment was evident in the 0–20, 20–40, and 40–60 mm soil depths; there was significant increase ($p \leq 0.05$) in Zn compared to treatments not receiving compost. The soil Zn concentration decreased with depth in all treatments during both years and was greater in 2018 than in 2017. The mean concentration difference was minimal at the surface layer but greater with depth, as was also observed with Cu. This suggests that although compost could bind limited amounts of Zn from wastewater, this element could still move deeper into the profile.

At the 30 cm depth, Cd, Cr, and Pb were <LOD but Cu, Fe, and Zn were present in both years; see Table A5. This could have been because Cu, Fe, and Zn are more mobile than Cd, Cr, and Pb. There were no differences in the concentration of Cu and Zn due to treatments ($p \leq 0.05$) in both years. Fe concentration was significantly lower ($p \leq 0.05$) in $BC_3CP_{7.5}$ compared to all other treatments.

3.3. Effect of Soil Amendments on Heavy Metals Uptake by Plant

The soil amendments affected the uptake of heavy metals by the potatoes. The concentration of Cd, Cu, and Zn in potato flesh, skin, roots, stems, and leaves for 2017 and 2018 are given in Tables 4 and 5. The concentrations of Cr, Pb, and Fe are given in Tables A6 and A7.

In both 2017 and 2018, Cd concentrations in the flesh, skin, and roots of the potatoes were significantly greater in the BC_0CP_0 treatment compared to other treatments, indicating that all amendments decreased Cd in the edible potato parts. In 2017, there were no significant differences in flesh Cd among the amendments; a similar trend was observed in potato skin, although the concentrations were greater under the BC_1CP_0 than the remaining amendment treatments. The Cd concentration in the roots was significantly greater ($p \leq 0.05$) under the BC_0CP_0 treatment than the other treatments. The stem concentration was significantly lower under the compost-amended treatments ($BC_0CP_{7.5}$, $BC_1CP_{7.5}$, and $BC_3CP_{7.5}$) compared to non-compost treatments, but there were no treatments effects for Cd concentration in leaves.

In 2018, the Cd concentration in flesh was significantly lower ($p \leq 0.05$) under compost-amended treatments than the only-biochar or no-biochar treatments. The flesh concentration under BC_0CP_0 was the highest, followed by BC_1CP_0 and BC_3CP_0. In potato skin, the Cd concentrations under BC_0CP_0 and BC_1CP_0 were significantly higher ($p \leq 0.05$) than under other treatments. Overall, Cd concentrations in roots and stems under the compost-amended treatments were significantly lower than those under the remaining treatments; however, no significant treatment effects were observed in leaves.

Table 4. Heavy metal concentrations (µg g^{-1}) in potato tissues in 2017. Values are the mean ± SD, *n* = 3.

Heavy Metal	Treatments	Flesh	Skin	Root	Stem	Leaves
Cd	BC_0CP_0	1.50 ± 0.96 ^{a}	11.29 ± 0.81 ^{a}	146.26 ± 16.54 ^{a}	14.04 ± 6.53 ^{a}	9.70 ± 2.49 ^{a}
	BC_1CP_0	1.07 ± 0.37 ^{ab}	7.35 ± 3.21 ^{ab}	68.52 ± 22.33 ^{b}	19.48 ± 7.04 ^{a}	6.12 ± 1.48 ^{a}
	BC_3CP_0	0.74 ± 0.13 ^{ab}	3.02 ± 0.82 ^{c}	68.33 ± 20.17 ^{b}	22.18 ± 13.53 ^{a}	4.65 ± 1.53 ^{a}
	$BC_0CP_{7.5}$	0.63 ± 0.06 ^{b}	2.29 ± 1.48 ^{c}	43.82 ± 34.73 ^{b}	9.98 ± 4.85 ^{b}	8.28 ± 5.87 ^{a}
	$BC_1CP_{7.5}$	0.63 ± 0.10 ^{b}	2.12 ± 1.18 ^{c}	43.29 ± 4.74 ^{b}	15.69 ± 6.48 ^{b}	8.40 ± 2.49 ^{a}
	$BC_3CP_{7.5}$	0.79 ± 0.16 ^{ab}	5.65 ± 2.75 ^{bc}	54.30 ± 26.96 ^{b}	10.44 ± 4.56 ^{b}	4.77 ± 1.64 ^{a}
Cu	BC_0CP_0	11.61 ± 1.73 ^{a}	10.9 ± 2.18 ^{ab}	39.54 ± 8.80 ^{a}	7.61 ± 2.67 ^{a}	19.00 ± 4.25 ^{a}
	BC_1CP_0	8.76 ± 1.83 ^{bc}	12.91 ± 2.65 ^{a}	39.34 ± 12.23 ^{a}	6.16 ± 2.41 ^{a}	9.73 ± 3.02 ^{abc}
	BC_3CP_0	6.70 ± 0.94 ^{c}	8.67 ± 0.78 ^{b}	39.94 ± 12.94 ^{a}	7.66 ± 4.43 ^{a}	6.24 ± 1.24 ^{c}
	$BC_0CP_{7.5}$	8.018 ± 1.01 ^{bc}	10.47 ± 2.2 ^{ab}	25.80 ± 17.57 ^{a}	7.61 ± 4.74 ^{a}	16.53 ± 10.04 ^{ab}
	$BC_1CP_{7.5}$	9.07 ± 0.50 ^{b}	10.69 ± 1.5 ^{ab}	30.63 ± 2.80 ^{a}	9.93 ± 6.52 ^{a}	15.64 ± 7.28 ^{abc}
	$BC_3CP_{7.5}$	6.82 ± 0.79 ^{c}	11.64 ± 2.6 ^{ab}	36.94 ± 6.78 ^{a}	4.51 ± 1.25 ^{a}	7.36 ± 0.79 ^{bc}
Zn	BC_0CP_0	19.61 ± 6.45 ^{a}	39.39 ± 12.72 ^{a}	217.36 ± 26.80 ^{a}	37.95 ± 7.82 ^{b}	13.97 ± 2.81 ^{a}
	BC_1CP_0	17.95 ± 2.34 ^{a}	32.63 ± 2.78 ^{ab}	166.16 ± 19.54 ^{b}	96.06 ± 32.49 ^{a}	9.89 ± 2.09 ^{a}
	BC_3CP_0	17.50 ± 2.23 ^{a}	21.52 ± 2.04 ^{c}	87.16 ± 18.35 ^{c}	55.71 ± 26.20 ^{ab}	9.93 ± 0.31 ^{a}
	$BC_0CP_{7.5}$	17.95 ± 5.06 ^{a}	21.21 ± 7.28 ^{c}	56.97 ± 0.19 ^{c}	65.35 ± 10.64 ^{ab}	13.59 ± 6.09 ^{a}
	$BC_1CP_{7.5}$	17.72 ± 1.16 ^{a}	21.22 ± 2.78 ^{c}	81.26 ± 10.05 ^{c}	59.38 ± 27.75 ^{ab}	11.35 ± 2.49 ^{a}
	$BC_3CP_{7.5}$	19.80 ± 4.13 ^{a}	25.08 ± 3.98 ^{bc}	72.25 ± 21.91 ^{c}	59.00 ± 29.67 ^{ab}	11.38 ± 0.83 ^{a}

$^{a–c}$ Within year, different letters in the same column for a given heavy metal indicate a significant difference ($p \leq 0.05$).

Table 5. Heavy metal concentrations (µg g^{-1}) in potato tissues in 2018. Values are the mean ± SD, *n* = 3.

Heavy Metal	Treatments	Flesh	Skin	Root	Stem	Leaves
Cd	BC_0CP_0	5.30 ± 1.37 ^{a}	59.36 ± 19.64 ^{a}	249.69 ± 43.02 ^{a}	24.77 ± 13.18 ^{ab}	15.35 ± 1.30 ^{a}
	BC_1CP_0	4.46 ± 1.79 ^{ab}	49.99 ± 6.98 ^{a}	223.76 ± 45.74 ^{a}	30.37 ± 7.52 ^{ab}	10.58 ± 1.70 ^{a}
	BC_3CP_0	3.06 ± 1.33 ^{bc}	12.61 ± 4.58 ^{b}	254.31 ± 25.42 ^{a}	32.64 ± 14.64 ^{a}	11.84 ± 6.61 ^{a}
	$BC_0CP_{7.5}$	1.30 ± 0.05 ^{c}	8.32 ± 6.37 ^{b}	46.31 ± 4.82 ^{b}	15.79 ± 6.10 ^{b}	9.90 ± 0.94 ^{a}
	$BC_1CP_{7.5}$	1.86 ± 0.57 ^{c}	7.43 ± 3.95 ^{b}	76.04 ± 22.56 ^{b}	15.28 ± 4.13 ^{b}	8.85 ± 2.40 ^{a}
	$BC_3CP_{7.5}$	1.16 ± 0.21 ^{c}	3.98 ± 0.52 ^{b}	100.29 ± 40.45 ^{b}	14.13 ± 1.03 ^{b}	10.10 ± 5.96 ^{a}
Cu	BC_0CP_0	10.8 ± 0.97 ^{ab}	23.50 ± 5.77 ^{ab}	72.35 ± 36.61 ^{ab}	12.88 ± 6.34 ^{a}	22.21 ± 6.74 ^{a}
	BC_1CP_0	11.2 ± 1.24 ^{ab}	23.93 ± 5.25 ^{a}	91.53 ± 45.00 ^{a}	11.25 ± 3.52 ^{a}	15.34 ± 1.47 ^{bc}
	BC_3CP_0	8.01 ± 0.71 ^{c}	15.93 ± 2.15 ^{ab}	60.92 ± 29.78 ^{ab}	6.13 ± 4.65 ^{a}	13.36 ± 2.70 ^{bc}
	$BC_0CP_{7.5}$	9.21 ± 1.25 ^{bc}	22.94 ± 5.81 ^{ab}	24.37 ± 4.88 ^{b}	12.66 ± 5.44 ^{a}	16.19 ± 4.31 ^{abc}
	$BC_1CP_{7.5}$	12.99 ± 2.31 ^{a}	19.72 ± 4.24 ^{ab}	66.46 ± 32.64 ^{ab}	9.25 ± 1.77 ^{a}	18.72 ± 2.52 ^{ab}
	$BC_3CP_{7.5}$	6.93 ± 1.05 ^{c}	15.49 ± 3.69 ^{b}	32.09 ± 17.66 ^{b}	6.22 ± 2.51 ^{a}	12.08 ± 1.22 ^{c}
Zn	BC_0CP_0	26.10 ± 3.51 ^{a}	101.46 ± 27.90 ^{a}	396.82 ± 27.27 ^{a}	93.64 ± 4.38 ^{a}	17.14 ± 1.74 ^{a}
	BC_1CP_0	23.83 ± 2.72 ^{ab}	82.70 ± 9.43 ^{a}	312.42 ± 51.88 ^{b}	116.38 ± 64.93 ^{a}	15.15 ± 1.43 ^{ab}
	BC_3CP_0	20.84 ± 1.59 ^{b}	41.16 ± 0.20 ^{b}	307.20 ± 39.76 ^{b}	91.52 ± 45.76 ^{a}	11.77 ± 1.36 ^{bc}
	$BC_0CP_{7.5}$	21.15 ± 2.20 ^{b}	44.65 ± 7.96 ^{b}	115.71 ± 13.23 ^{c}	100.11 ± 37.03 ^{a}	13.95 ± 3.28 ^{abc}
	$BC_1CP_{7.5}$	22.03 ± 1.33 ^{ab}	37.77 ± 4.99 ^{b}	115.31 ± 35.20 ^{c}	75.08 ± 14.08 ^{a}	13.54 ± 3.12 ^{abc}
	$BC_3CP_{7.5}$	19.86 ± 3.86 ^{b}	34.88 ± 12.03 ^{b}	122.70 ± 41.77 ^{c}	55.88 ± 18.85 ^{a}	10.83 ± 1.92 ^{c}

$^{a–c}$ Within year, different letters in the same column indicate a significant difference ($p \leq 0.05$).

These results indicate that the compost amendment reduced Cd uptake into the edible portions of the potato, as well as the roots and stems. There was slight reduction in Cd uptake with the 3% biochar amendment, but a minimal effect was evident with the 1% biochar amendment. It may be noted that the topsoil Cd concentrations in treatments with compost were higher than those under other treatments. Despite this, the uptake was low, which indicates that compost reduced Cd bioavailability while increasing soil adsorption.

Similar to soil mobility, neither biochar or compost (or both) had any effects on the uptake of soil Cr and Pb into potatoes; see Tables A6 and A7. Exceptionally in 2018, compared to the BC_0CP_0 control, soil amended with BC_3CP_0 reduced ($p \leq 0.05$) root Cr, but root Pb ($p \leq 0.05$) was greater under $BC_1CP_{7.5}$ than under BC_3CP_0, $BC_0CP_{7.5}$, and $BC_3CP_{7.5}$. Among Cd, Cr, and Pb, compost appeared to be most effective at reducing Cd uptake.

While Cd, Cr, and Pb are toxic heavy metals, Cu, Fe, and Zn are trace elements required by crops; however, their excessive presence in soil and uptake by plants can be toxic to plants and humans consuming such plants. The concentration of these heavy metals in the plant parts are given in Tables 4, 5, A6 and A7.

In 2017, the Cu concentration in potato flesh under the non-amendment treatment was significantly greater ($p \leq 0.05$) than under amended treatments. Moreover, there was significant effect of the biochar amendment, and the effect increased with the quantity of biochar; the Cu flesh concentration under the BC_3CP_0 treatment was slightly lower than that under BC_1CP_0 and significantly lower under $BC_3CP_{7.5}$ than under $BC_1CP_{7.5}$. The $BC_0CP_{7.5}$ treatment showed significantly lower soil Cu than the non-amended BC_0CP_0 treatment; however, there were no differences between $BC_1CP_{7.5}$ and BC_1CP_0 or between $BC_3CP_{7.5}$ and BC_3CP_0. These results suggest that biochar played the biggest role in reducing flesh Cu.

In 2018, there were also significantly lower concentrations of flesh Cu for 3% biochar with or without compost than under the remaining treatments, but there was no difference between those two treatments. This indicated that 3% biochar was effective in reducing Cu bioavailability. As was observed in 2017, Cu in leaves was significantly lower under $BC_3CP_{7.5}$ and significantly higher under BC_0CP_0 compared to the remaining treatments. These findings suggest that the transport of Cu to leaves may decrease with soil amendments of compost and a high rate of biochar. There were no conclusive differences between treatments for skin, roots, and stems for both years.

In 2017, no significant effect of treatment was found on Fe concentration in any potato parts, whereas in 2018, Fe concentration was significantly lower in flesh and roots under $BC_3CP_{7.5}$ than under BC_0CP_0. Overall, there was no conclusive evidence of any effect of soil amendment on the bioavailability of Fe in potatoes.

Similarly, there was no effect of amendments on the concentration of Zn in potato flesh, though the Zn concentrations in skin and roots were significantly higher ($p \leq 0.05$) in BC_0CP_0 than in all amendment treatments. In 2018, Zn concentrations in potato flesh and skin were significantly lower in treatments with compost and high biochar content than under the non-amended control. Zn concentrations in roots and stems were not affected by treatments, as both amendments reduced Zn uptake. Overall, the treatments had the greatest effects on the plant uptake of Cd and Cu.

4. Discussion

4.1. Effect of Soil Amendments on Soil Properties and Heavy Metal Mobility

Earlier studies have shown that compost amendment improves soil CEC [24–26]. Compost increases the CEC since it increases the soil exchange sites through the addition of stabilized organic matter rich in functional phenolic and carboxylic acid groups [51,52]. We also corroborated this finding.

Regarding biochars, those produced at low (<350 °C) temperatures have higher CEC values than those produced at higher temperatures due to higher surface area and greater number of oxygen functional groups [53,54]. Basso et al. [55] showed that a moderate-temperature, fast-pyrolysis (500 °C) hardwood biochar applied at 3% and 6% (w/w) had no effect on the CEC of a sandy soil. Our study mirrored these results, as soils amended with compost had greater ($p \leq 0.05$) CEC values than other treatments, while 1% biochar alone (produced at 535 °C) had no effect and 3% biochar alone had a minimal effect. As for heavy metal immobilization, the application of compost, alone or with biochar, increased the soil CEC, thus enhancing the retention of metals in topsoil. The increased soil CEC was likely a consequence of elements released from the compost and biochar when co-amended with the soil. As a result, though the total concentration of metals in the soil remained unchanged during the remediation process, their bioavailability was substantially reduced due to the increased CEC. This result concurs with the work of Kargar et al. [25], who found that soil amendments with compost significantly increased the soil's sorption and retention capacity for trace metals. They suggested that the CEC was the main mechanism for controlling the mobility of Cd and Zn in soils. Moreover, Kargar et al. [25] saw a positive relationship between exchangeable Ca and Mg and compost application rates. Zn and Cd concentrations were shown to be negatively correlated with soil leachate's exchangeable cations (Ca^{2+} and Mg^{2+}), supporting the idea that an increasing CEC is the main mechanism controlling Zn and Cd mobility [56].

As the most mobile carbon fraction, DOC plays a crucial role in influencing soil processes such as nutrient availability and leaching [57], thereby playing an important role in soil contaminants' mobility and bioavailability [58,59]. Soil DOC concentration has been linked to the formation of soluble organo–metallic complexes that may prevent plants' absorption of metals [24]. Greater DOC values have been linked to increased surfaces for metal sorption, reducing the availability of heavy metals to plants; Beesley et al. [60] reported that DOC controlled metal mobility after compost amendment. According to Karami et al. [61], most of the soil's heavy metal pool is complexed by DOC in the presence of compost, and this is more so for Pb and Cu than Zn and Cd. On the other hand, biochar treatment does not enhance metal complexation in pore water to the same extent as compost, which may explain its more effective retention of metals in solid phases. However, compost amendments have also been seen to increase soil Cd, Cu, and Zn concentrations [24], which support our findings that the compost amendment enhanced the retention of heavy metals in the soil.

Soil pH has a strong inverse relationship with trace metals' solubility and mobility (i.e., low metal solubility at high pH and high metal solubility at low pH) [62,63], making pH the most significant factor in a metallic element's environmental fate [64,65]. Therefore, the soil's pH is key to heavy metal adsorption and can take precedence over the complex surface reactions of cations, anions, and other metal-binding mechanisms [18,61]. After mixing compost into soil, soil pH can increase due to carbon mineralization and the subsequent production of hydroxyl ions by the exchange of ligands and the introduction of basic cations, such as K^{+}, Ca^{2+}, and Mg^{2+} [66], as was shown in this study. Studies have found that biochars originating from different feedstocks can also increase soil pH to different extents [20,67]; the effects of barley straw biochar observed in our study corroborated their findings.

The pH of the pre-treatment soil and the wastewater were mildly acidic in our study. Compared to the non-amended and 1% biochar treatments, compost and 3% biochar increased soil pH in the root zone (0–100 mm). These results agree with the work of Oustriere et al. [26], who found that the application of biochar together with compost could effectively reduce soil leaching of Cd, Zn, and Pb through increased-pH-driven precipitation–co-precipitation and various sorption mechanisms. Moreover, in investigating the effects of increasing soil pH, Friesl-Hanl et al. [68] and Friesl et al. [69] found that a higher soil pH could promote Pb retention in the soil's solid phase. In our study, the CEC, DOC and pH increased when compost (with or without biochar) or 3% biochar alone was amended. Increases in these parameters enhanced the adsorption of Cd, Cu, and Zn in our study, likely through precipitation.

Our findings contrast in part with those of Gusiatin and Kulikowska [70], who reported that sewage sludge compost decreased the bioavailability of soil Cd and Zn but did not affect the availability of Pb or Cu. Similarly, Tang et al. [71] found that compost, obtained from agricultural waste, substantially reduced the availability of soil Cd and Zn but increased the availability of soil Cu. In another study, it was found that plantain peel biochar mixed with hydrogel reduced the transport of heavy metals—Cd, Cu, Fe, and Zn—and retained significantly higher amounts added from wastewater irrigation [13]. Nzediegwu et al. [72] also reported that plantain peel biochar significantly increased the retention of Cd and Zn in the top 0.05 m depth and also retained considerably higher amounts of Cr, Cu, Fe, and Pb. Dhiman et al. [13] and Nzediegwu et al. [72] attributed the effectiveness of biochar to higher CEC values. Our experiment also indicated that barley straw biochar retained a significantly higher amount of Cd in the surface soil. Biochar and compost did not impact the mobility of Cr and Pb in the soil, though they did restrict the mobility of Cd. This is likely attributable to differences in metals' characteristics and competitiveness towards binding sites [73–75].

It appears that biochar could not restrict the transport of Fe, Cu, and Zn (minor essential elements for crop growth), although compost exhibited positive effect for Cu and Zn. According to Beesley et al. [18], a combination of compost with biochar as a soil amendment may be more suitable than biochar alone to promote heavy metal immobilization and buffer nutrient depletion in contaminated soils. Our study showed that barley straw biochar, if applied at the rate of 3%, reduced the transport of Cd, although 1% biochar was not effective. Overall, increases in soil heavy metal retention in amended soil are likely due to the enhancement of the soil physicochemical parameters such as the CEC, DOC, and pH, as was associated with the $BC_0CP_{7.5}$, $BC_1CP_{7.5}$, and $BC_3CP_{7.5}$ compost treatments in the present study. Increasing pH from acidic to neutral can affect metal speciation, causing heavy metals to precipitate.

Most soil Pb is concentrated in the topsoil (0–20 mm), suggesting that Pb adsorption in soils may be permanent and irreversible [76]. Although Pb was detected at soil depths of 30–40, 40–60, and 80–100 mm in both years of this study, the concentration was within the permissible limit for Pb in an agricultural soil (<70 mg kg^{-1}) set by the Canadian Soil Quality Guidelines [77]. Although Zn was detected at all soil depths in both years, the concentration was within the Canadian Soil Quality Guidelines' permissible limits for agricultural soil (200 mg kg^{-1}) [77].

4.2. Effect of Soil Amendments on Heavy Metal Uptake by Plant

In terms of bioavailability, our findings are consistent with previously observed reductions in Cd content in dwarf beans [26] and potatoes [78] as a result of compost and biochar amendment, suggesting that a combination of biochar and compost is more efficient in reducing Cd uptake than biochar alone. Such a combination could synergistically affect soil physicochemical properties, including the CEC and pH, reducing metal availability to plants. While the Cd concentration in the flesh of wastewater-irrigated potatoes exceeded the permissible limit of 0.1 mg kg^{-1} [79], both the $BC_0CP_{7.5}$ and $BC_1CP_{7.5}$ treatments greatly decreased potato flesh Cd in both years compared to the non-amended soil. This is likely the result of the fact that compost is more effective than biochar in reducing Cd translocation from the soil to plants.

Several studies have considered the impact of biochar on Cd. Khan et al. [20] found that the concentrations of Cd in pak choi (*Brassica rapa* ssb. *chinensis* L.) were significantly reduced by the addition of 5% (vs. 2.5%) biochar, but the reduction varied according to the biochar feedstock (green tomato waste, chicken manure, duck manure, barley straw, or swine manure), suggesting the importance of determining the optimal quantity of various biochars to apply as a soil amendment so that the crop uptake of heavy metal contaminants is minimized while yield is maintained. In our study, we also saw significant reductions in skin (2017 and 2018) and flesh Cd (2018) with 3% biochar; however, these impacts were also seen in all treatments with compost.

Kocasoy and Güvener [17] observed that compost was not effective in adsorbing Cr. In our study, municipal waste compost was also ineffective in adsorbing or reducing the uptake of Cr. Antonious and Snyder [80] reported that compost had no effect on Cr concentration in potato tubers in either Cr-contaminated or non-contaminated soils, suggesting that those potatoes would uptake a certain amount of Cr irrespective of concentration in soil. Dhiman et al. [13] also found no significant effects on Cr concentration in the flesh of potatoes irrigated with wastewater and grown in soil amended with a polyacrylamide super absorbent polymer alone or mixed with plantain peel biochar.

Milojković et al. [81] reported that compost produced from aquatic weeds could remove Pb from water. Karami et al. [61] found that a compost and biochar combination showed comparable reductions of Pb in soil pore water compared to compost alone, though biochar alone was not as effective. In the present study, potato tubers accumulated minimal quantities of Cr and Pb after wastewater irrigation, irrespective of treatments. Other studies have also shown the translocation of soil Cr and Pb to plants to be very poor [82,83]. In contrast to our results, Oustriere et al. [26] found that both pine bark biochar and green waste compost amendments reduced Pb uptake by dwarf beans, while Eissa [84] obtained similar results for Old Man Saltbush [84]. This trend was attributed to the fact that Pb was retained in the topsoil and did not move down to the root zone. In the present study, there was no apparent effect of either barley straw biochar or municipal waste compost on reducing Pb uptake. In 2017, Pb in potato flesh was marginally higher than the permissible limit of 0.1 mg kg^{-1} [79].

Concurring with our findings, Chen et al. [85] reported that soil amendment with compost of wheat straw biochar with different rates reduced the bioavailability of Cu. Soja et al. [86] also reported that biochar was effective in immobilizing Cu, especially in acidic soils. They suggested that the impact of biochar and compost in a Cu-enriched vineyard, in terms of Cu immobilization in the topsoil, may depend on either the immobilizing ability of the DOC in the compost fraction or the sorption potential of biochar. However, the soil was mostly acidic in all the treatments, so the effect of biochar was prominent. Generally, there are no effects of compost on Cu dynamics [87]. Kargar et al. [88] also reported that a compost amendment had no significant effects on Cu uptake by barley. Similar to our results, Seguin et al. [89] found that Cu bioavailability decreased with an increase in biochar amendment rates. The reductions in Cu bioavailability in the $BC_3CP_{7.5}$ amendment were consistent with the results reported by Jones et al. [11], who found that a soil amendment with biochar and compost significantly reduced the mobility and plant uptake of Cu. Moreover, the most significant reductions in leachable and plant uptake Cu were associated with the greatest biochar application rates in combination with compost.

As in our study, Nzediegwu et al. [14,72] found no effect of plantain peel biochar on the translocation of Fe to potato tissues in a two-year wastewater irrigation study. Moreover, similar to our findings, Tahir et al. [90] found the Fe concentration in spinach to not be affected by biochar amendment or by its co-amendment with different rates of manure. Our findings contrast those of Al Mamun et al. [78], who found the Fe concentration in potato skin to be reduced by the amendment of various composts derived from pig manure, mushrooms, sawdust-animal waste, and municipal waste. Likewise, Jones et al. [11] found three biochar and compost soil amendments to increase Fe concentration in sunflower shoots.

Egene et al. [24] concluded that although compost amendments could retain Zn in soil and thereby decrease Zn uptake, some decreases in Zn uptake were observed due to both biochar and compost. Similarly, Angelova et al. [91] found that compost treatment decreased Zn concentration in potato tubers but had no effect on the other plant parts. Similar reductions in Zn concentrations were also reported for switchgrass by beef cattle manure biochar and compost amendment [92] and Chinese cabbage [93] as a result of soil wheat straw biochar/compost amendments.

Karer et al. [94] found positive effects of a biochar–compost mix on soil Zn concentration and plant uptake in *Miscanthus* × *giganteus* shoots under greenhouse and field conditions. Similarly, Liang et al. [95] studied the effects of a combination of compost and rice husk biochar at varying application rates on Zn availability. They found that available Zn declined under the 10% and 20% biochar amendments due to changes in pH. Overall, the compost and biochar amendments have been shown to reduce the uptake of Cd, Cu, and Zn. Compost was found to mainly reduce Cd uptake, whereas barley straw biochar was found to be effective in reducing the uptake of Cu. To some extent, both compost and barley straw biochar were shown to reduce the uptake of Zn.

5. Conclusions

Soil amendments with barley straw biochar, alone or supplemented with city green and table waste compost, retained the wastewater-borne heavy metals Cd, Cu, and Zn in the topsoil and reduced their uptake by potato plants for two years, depending on biochar application rate and the heavy metal type. Relative to non-amended soils and soils amended at 1%, amending the soils with barley straw biochar at 3% was more effective in reducing heavy metals' transport in soil and their uptake by plants. An amendment with green and table waste compost reduced the transport of Cd and Zn relative to the non-amended control, and such reduction was further enhanced when the compost was mixed with biochar due to the synergistic effects of the combination. Therefore, co-adding biochar and compost to soil under wastewater irrigation can reduce the potential hazard posed by wastewater-borne heavy metals, especially Cd, Cu, and Zn, to potato crops. We recommend a long-term study on heavy metal uptake by plants and immobilization in soils amended with biochar and compost in order to fully understand the sustainability of these techniques in wastewater irrigation.

Author Contributions: A.M., experimental design, conducting all experiments, data collection, analysis, interpretation of data, and writing—original draft. S.O.P. was a research supervisor and involved in funding acquisition, conceptualization, project administration, methodology, resources, supervision, and writing—review and editing. S.B., was a research co-supervisor, provided invaluable scientific and technical advice, and was actively involved in every stage of the study including data curation, validation, and writing—review and editing. E.C.A., C.N. and R.P. were involved in methodology and writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Appendix A

Table A1. Properties of barley straw biochar (BC) and mixed green and table waste compost (CP).

Parameter	Value (%, *w*/*w*)		Element Concentrations (mg kg^{-1})			* Allowable Thresholds (mg kg^{-1})	
	BC	CP	Element	BC	CP	BC	CP
Moisture TGA	3.88	4.38	Cd	<LOD	<LOD	1.40	20.00
Ash TGA	19.29	64.43	Cr	29.80	19.91	64	1060
Volatile Matter	18.19	29.09	Cu	<LOD	44.22	63	757
Fixed Carbon	62.53	6.47	Fe	706.71	8205.25	NA	NA
Carbon	70.40	18.80	Pb	<LOD	<LOD	70	505
Hydrogen	2.20	1.83	Zn	33.11	90.01	200	1850
Nitrogen	1.07	1.28	N	5.12	36.81	NA	NA
Total Sulfur	0.53	0.16	P	244.02	763.72	NA	NA
Oxygen	6.47	13.47	K	18,201.05	4324.15	NA	NA
SSA (m^2 g^{-1})	8.5	2.05	Mg	520.23	1008.01	NA	NA
pH	9.61	7.87	Ca	750.09	4991.21	NA	NA
EC (mS cm^{-1})	4302.02	1226.61	Mn	40.02	40.15	NA	NA

TGA: thermogravimetric analysis; SSA: specific surface area; EC: electrical conductivity; NA: not available; * Based on International Biochar Initiative allowable thresholds of heavy metals in biochar and Guidelines for Compost Quality Canadian Council of Ministers of the Environment [96] (mg kg^{-1}).

Table A2. Cr concentration (mg kg^{-1}) in different soil layers on the day of harvest in 2017 and 2018. Values are the mean ± SD, *n* = 3.

Treatments	0–2 cm	2–4 cm	4–6 cm	6–8 cm	8–10 cm
			2017		
BC_0CP_0	60.10 ± 2.10 ^{a}	42.42 ± 12.15 ^{a}	25.67 ± 8.84 ^{a}	24.06 ± 1.89 ^{a}	20.58 ± 1.45 ^{a}
BC_1CP_0	60.77 ± 6.60 ^{a}	36.31 ± 5.69 ^{a}	20.52 ± 2.45 ^{a}	25.44 ± 5.62 ^{a}	21.23 ± 1.06 ^{a}
BC_3CP_0	64.92 ± 8.78 ^{a}	32.58 ± 9.89 ^{a}	23.62 ± 2.35 ^{a}	24.48 ± 4.32 ^{a}	19.34 ± 0.64 ^{a}
$BC_0CP_{7.5}$	66.73 ± 21.54 ^{a}	31.99 ± 4.84 ^{a}	21.97 ± 1.12 ^{a}	23.15 ± 3.94 ^{a}	22.81 ± 1.31 ^{a}
$BC_1CP_{7.5}$	90.46 ± 23.38 ^{a}	31.55 ± 3.96 ^{a}	24.83 ± 3.52 ^{a}	26.11 ± 5.63 ^{a}	22.41 ± 3.44 ^{a}
$BC_3CP_{7.5}$	90.94 ± 38.87 ^{a}	41.17 ± 13.70 ^{a}	23.23 ± 1.98 ^{a}	23.89 ± 5.25 ^{a}	22.01 ± 5.46 ^{a}
			2018		
BC_0CP_0	30.60 ± 2.78 ^{a}	33.02 ± 9.01 ^{a}	29.51 ± 3.41 ^{bc}	27.14 ± 2.37 ^{a}	23.42 ± 2.39 ^{bc}
BC_1CP_0	34.70 ± 5.34 ^{a}	32.52 ± 6.44 ^{a}	32.87 ± 4.63 ^{bc}	32.65 ± 6.73 ^{a}	26.55 ± 2.14 ^{ab}
BC_3CP_0	35.03 ± 9.15 ^{a}	29.13 ± 3.01 ^{a}	26.14 ± 4.08 ^{c}	24.76 ± 6.30 ^{a}	22.44 ± 3.11 ^{bc}
$BC_0CP_{7.5}$	39.36 ± 3.52 ^{a}	36.04 ± 6.67 ^{a}	41.50 ± 2.85 ^{a}	35.13 ± 3.30 ^{a}	24.56 ± 1.14 ^{ab}
$BC_1CP_{7.5}$	41.25 ± 8.99 ^{a}	37.92 ± 2.25 ^{a}	36.10 ± 5.49 ^{ab}	39.15 ± 15.97 ^{a}	28.48 ± 2.17 ^{ab}
$BC_3CP_{7.5}$	37.99 ± 5.65 ^{a}	34.30 ± 6.87 ^{a}	33.94 ± 6.65 ^{abc}	36.83 ± 9.34 ^{a}	30.89 ± 7.55 ^{a}

$^{a–c}$ Within year, different letters in the same column indicate a significant difference ($p \leq 0.05$).

Table A3. Pb concentration (mg kg^{-1}) in different soil layers on the day of harvest in 2017 and 2018. Values are the mean ± SD, *n* = 3.

Treatments	0–2 cm	2–4 cm	4–6 cm	6–8 cm	8–10 cm
			2017		
BC_0CP_0	292.00 ± 6.88 ^{a}	172.96 ± 111.01 ^{a}	10.77 ± 0.82 ^{c}	28.54 ± 3.75 ^{a}	<LOD
BC_1CP_0	319.80 ± 39.43 ^{a}	122.97 ± 41.06 ^{a}	23.53 ± 2.60 ^{abc}	30.03 ± 22.08 ^{a}	<LOD
BC_3CP_0	354.86 ± 37.47 ^{a}	109.92 ± 54.42 ^{a}	32.05 ± 17.91 ^{ab}	44.51 ± 18.54 ^{a}	<LOD
$BC_0CP_{7.5}$	357.89 ± 136.83 ^{a}	43.85 ± 5.69 ^{a}	23.68 ± 3.86 ^{abc}	23.90 ± 7.70 ^{a}	<LOD
$BC_1CP_{7.5}$	512.71 ± 163.66 ^{a}	116.12 ± 74.16 ^{a}	36.34 ± 16.16 ^{a}	44.21 ± 24.96 ^{a}	<LOD
$BC_3CP_{7.5}$	478.87 ± 183.55 ^{a}	139.99 ± 97.67 ^{a}	15.78 ± 2.08 ^{bc}	24.60 ± 19.00 ^{a}	<LOD
			2018		
BC_0CP_0	366.91 ± 75.91 ^{b}	131.77 ± 113.43 ^{a}	144.45 ± 150.17 ^{a}	73.84 ± 38.46 ^{ab}	37.93 ± 29.67 ^{a}
BC_1CP_0	345.32 ± 45.81 ^{b}	230.55 ± 259.36 ^{a}	59.17 ± 47.10 ^{a}	88.19 ± 75.93 ^{ab}	38.89 ± 39.80 ^{a}
BC_3CP_0	383.83 ± 118.61 ^{b}	131.31 ± 134.81 ^{a}	42.78 ± 29.08 ^{a}	29.13 ± 21.77 ^{b}	7.60 ± 2.83 ^{a}
$BC_0CP_{7.5}$	456.28 ± 180.58 ^{b}	179.42 ± 72.22 ^{a}	178.48 ± 88.65 ^{a}	87.25 ± 50.13 ^{ab}	23.01 ± 16.62 ^{a}
$BC_1CP_{7.5}$	556.85 ± 166.02 ^{ab}	330.90 ± 112.52 ^{a}	167.98 ± 110.62 ^{a}	163.29 ± 96.02 ^{a}	110.85 ± 176.82 ^{a}
$BC_3CP_{7.5}$	724.91 ± 133.58 ^{a}	150.97 ± 110.91 ^{a}	191.96 ± 62.72 ^{a}	148.18 ± 18.68 ^{a}	29.35 ± 33.96 ^{a}

<LOD: means below the limit of detection. $^{a–c}$ Within year, different letters in the same column indicate a significant difference ($p \leq 0.05$).

Table A4. Fe concentration (mg kg^{-1}) in different soil layers on the day of harvest in 2017 and 2018. Values are the mean ± SD, *n* = 3.

Treatments	0–2 cm	2–4 cm	4–6 cm	6–8 cm	8–10 cm
			2017		
BC_0CP_0	15,424.44 ± 305.48 ^{a}	15,584.31 ± 410.82 ^{a}	14,815.54 ± 1158.52 ^{a}	13,757.77 ± 879.31 ^{a}	12,296.06 ± 1384.47 ^{a}
BC_1CP_0	15,638.91 ± 1229.95 ^{a}	15,484.50 ± 423.90 ^{a}	13,184.62 ± 483.58 ^{a}	14,213.65 ± 983.29 ^{a}	13,620.87 ± 934.55 ^{a}
BC_3CP_0	14,899.25 ± 707.55 ^{a}	14,082.52 ± 2417.82 ^{a}	14,381.73 ± 1195.88 ^{a}	12,688.85 ± 2433.57 ^{a}	11,820.13 ± 769.12 ^{a}
$BC_0CP_{7.5}$	15,707.36 ± 1024.78 ^{a}	14,612.88 ± 642.89 ^{a}	13,335.80 ± 959.10 ^{a}	12,790.16 ± 1299.73 ^{a}	13,514.55 ± 757.46 ^{a}
$BC_1CP_{7.5}$	16,545.92 ± 756.84 ^{a}	14,592.07 ± 468.43 ^{a}	13,356.42 ± 837.48 ^{a}	13,357.83 ± 801.69 ^{a}	12,428.86 ± 247.42 ^{a}
$BC_3CP_{7.5}$	16,126.18 ± 1051.67 ^{a}	16,235.98 ± 651.43 ^{a}	13,230.18 ± 986.85 ^{a}	14,254.73 ± 2597.80 ^{a}	13,042.83 ± 2498.00 ^{a}
			2018		
BC_0CP_0	15,766.43 ± 2054.19 ^{a}	14,398.20 ± 1340.50 ^{bc}	14,795.42 ± 1535.24 ^{ab}	13,468.15 ± 385.03 ^{ab}	12,657.73 ± 631.50 ^{ab}
BC_1CP_0	15,589.19 ± 1383.89 ^{a}	14,574.01 ± 1386.05 ^{b}	14,216.98 ± 1453.63 ^{ab}	14,052.59 ± 1426.64 ^{a}	13,623.98 ± 311.68 ^{ab}
BC_3CP_0	15,287.49 ± 3444.10 ^{a}	12,887.64 ± 834.86 ^{c}	13,047.33 ± 512.72 ^{b}	11,618.55 ± 577.17 ^{b}	12,117.48 ± 1068.98 ^{b}
$BC_0CP_{7.5}$	16,938.51 ± 1454.31 ^{a}	14,872.43 ± 263.44 ^{ab}	15,342.64 ± 1271.16 ^{a}	13,276.33 ± 646.01 ^{ab}	12,677.46 ± 1256.38 ^{ab}
$BC_1CP_{7.5}$	16,477.21 ± 491.24 ^{a}	16,248.04 ± 339.57 ^{a}	14,650.58 ± 1725.93 ^{ab}	13,947.65 ± 1831.53 ^{a}	13,761.56 ± 1047.86 ^{a}
$BC_3CP_{7.5}$	16,671.64 ± 739.49 ^{a}	14,157.63 ± 411.40 ^{bc}	14,328.70 ± 542.76 ^{ab}	13,680.20 ± 569.25 ^{a}	12,154.92 ± 832.70 ^{ab}

$^{a–c}$ Within year, different letters in the same column indicate a significant difference ($p \leq 0.05$).

Table A5. Cu, Fe, and Zn concentrations (mg kg^{-1}) in 30 cm depth on the day of harvest in 2017 and 2018. Values are the mean ± SD, $n = 3$.

Treatments	Cu	Fe	Zn
		2017	
BC_0CP_0	59.94 ± 4.73 [a]	10,300.64 ± 562.33 [a]	23.03 ± 4.39 [a]
BC_1CP_0	54.61 ± 14.27 [a]	10,517.90 ± 1130.49 [a]	27.81 ± 1.99 [a]
BC_3CP_0	71.79 ± 23.97 [a]	10,562.97 ± 1144.02 [a]	26.33 ± 1.34 [a]
$BC_0CP_{7.5}$	52.87 ± 3.85 [a]	10,042.56 ± 1215.49 [a]	25.53 ± 3.76 [a]
$BC_1CP_{7.5}$	59.31 ± 24.24 [a]	12,353.07 ± 1050.01 [a]	27.93 ± 4.92 [a]
$BC_3CP_{7.5}$	89.08 ± 19.83 [a]	10,259.12 ± 670.99 [a]	32.35 ± 6.27 [a]
		2018	
BC_0CP_0	67.71 ± 15.21 [a]	10,318.95 ± 774.80 [ab]	24.83 ± 3.22 [a]
BC_1CP_0	62.87 ± 18.84 [a]	12,403.26 ± 1802.17 [a]	31.89 ± 1.35 [a]
BC_3CP_0	61.87 ± 14.31 [a]	11,608.67 ± 1179.99 [ab]	25.22 ± 5.28 [a]
$BC_0CP_{7.5}$	79.29 ± 31.17 [a]	10,049.01 ± 622.05 [ab]	24.19 ± 2.21 [a]
$BC_1CP_{7.5}$	59.88 ± 4.92 [a]	10,632.91 ± 507.26 [ab]	24.34 ± 2.09 [a]
$BC_3CP_{7.5}$	68.14 ± 20.76 [a]	9588.95 ± 365.98 [b]	24.66 ± 2.24 [a]

[a,b] Within year, different letters in the same column indicate a significant difference ($p \leq 0.05$).

Table A6. Heavy metal concentrations (μg g^{-1}) in potato tissues in 2017. Values are the mean ± SD, $n = 3$.

Heavy Metal	Treatments	Flesh	Skin	Root	Stem	Leaves
Cr	BC_0CP_0	0.10 ± 0.00 [a]	0.27 ± 0.05 [b]	2.09 ± 0.13 [b]	0.42 ± 0.00 [ab]	2.66 ± 1.24 [ab]
	BC_1CP_0	0.25 ± 0.17 [a]	0.60 ± 0.17 [a]	1.83 ± 0.49 [b]	0.35 ± 0.10 [b]	0.49 ± 0.23 [b]
	BC_3CP_0	0.20 ± 0.04 [a]	0.21 ± 0.04 [b]	2.62 ± 0.44 [ab]	0.80 ± 0.62 [ab]	0.75 ± 0.34 [b]
	$BC_0CP_{7.5}$	0.28 ± 0.18 [a]	0.36 ± 0.09 [b]	2.22 ± 1.20 [ab]	0.22 ± 0.10 [b]	4.65 ± 0.66 [a]
	$BC_1CP_{7.5}$	0.22 ± 0.03 [a]	0.45 ± 0.15 [ab]	2.73 ± 1.28 [ab]	2.14 ± 1.77 [a]	4.47 ± 3.46 [a]
	$BC_3CP_{7.5}$	0.17 ± 0.09 [a]	0.44 ± 0.11 [ab]	3.59 ± 0.38 [a]	0.45 ± 0.19 [b]	0.91 ± 0.38 [b]
Pb	BC_0CP_0	0.24 ± 0.17 [ab]	0.41 ± 0.22 [b]	27.12 ± 3.02 [a]	2.55 ± 0.19 [a]	19.54 ± 10.47 [a]
	BC_1CP_0	0.08 ± 0.03 [b]	1.38 ± 0.59 [a]	26.46 ± 9.99 [a]	2.51 ± 1.09 [a]	5.04 ± 5.36 [a]
	BC_3CP_0	0.22 ± 0.146 [ab]	0.39 ± 0.08 [ab]	29.29 ± 10.02 [a]	5.61 ± 4.08 [a]	3.11 ± 2.06 [a]
	$BC_0CP_{7.5}$	0.04 ± 0.01 [b]	1.17 ± 0.95 [ab]	12.43 ± 1.13 [a]	1.35 ± 1.18 [a]	21.21 ± 17.86 [a]
	$BC_1CP_{7.5}$	0.35 ± 0.01 [a]	1.34 ± 0.19 [ab]	27.54 ± 9.80 [a]	9.37 ± 8.68 [a]	19.69 ± 21.57 [a]
	$BC_3CP_{7.5}$	0.29 ± 0.04 [a]	1.56 ± 0.24 [a]	34.01 ± 9.13 [a]	2.50 ± 2.21 [a]	4.46 ± 2.21 [a]
Fe	BC_0CP_0	22.51 ± 5.21 [a]	77.4 ± 21.06 [a]	405.04 ± 45.93 [a]	44.01 ± 3.74 [a]	306.97 ± 115.31 [a]
	BC_1CP_0	23.09 ± 7.61 [a]	80.16 ± 29.5 [a]	401.97 ± 185.15 [a]	46.27 ± 24.10 [a]	190.29 ± 62.08 [a]
	BC_3CP_0	21.55 ± 0.65 [a]	67.10 ± 23.0 [a]	375.04 ± 60.40 [a]	69.15 ± 35.61 [a]	145.64 ± 24.21 [a]
	$BC_0CP_{7.5}$	22.23 ± 1.23 [a]	51.54 ± 15.4 [a]	257.03 ± 54.70 [a]	24.38 ± 8.85 [a]	310.61 ± 212.25 [a]
	$BC_1CP_{7.5}$	27.25 ± 5.38 [a]	55.38 ± 21.3 [a]	359.00 ± 93.70 [a]	86.21 ± 64.66 [a]	202.26 ± 105.93 [a]
	$BC_3CP_{7.5}$	23.30 ± 3.80 [a]	44.66 ± 8.51 [a]	344.90 ± 42.87 [a]	32.86 ± 12.27 [a]	162.71 ± 32.01 [a]

[a,b] Within year, different letters in the same column for a given heavy metal indicate a significant difference ($p \leq 0.05$).

Table A7. Heavy metal concentrations (μg g^{-1}) in potato tissues in 2018. Values are the mean ± SD, $n = 3$.

Heavy Metal	Treatments	Flesh	Skin	Root	Stem	Leaves
Cr	BC_0CP_0	0.04 ± 0.01 [a]	0.37 ± 0.04 [ab]	2.79 ± 0.90 [a]	0.26 ± 0.16 [a]	0.37 ± 0.11 [a]
	BC_1CP_0	0.09 ± 0.08 [a]	0.28 ± 0.01 [abc]	1.86 ± 1.04 [ab]	0.15 ± 0.04 [a]	0.26 ± 0.05 [a]
	BC_3CP_0	0.06 ± 0.01 [a]	0.21 ± 0.10 [c]	1.55 ± 0.36 [b]	0.24 ± 0.08 [a]	0.27 ± 0.14 [a]
	$BC_0CP_{7.5}$	0.04 ± 0.00 [a]	0.43 ± 0.14 [a]	1.97 ± 0.49 [ab]	0.06 ± 0.01 [a]	0.33 ± 0.07 [a]
	$BC_1CP_{7.5}$	0.05 ± 0.00 [a]	0.41 ± 0.05 [a]	2.48 ± 0.36 [ab]	0.39 ± 0.37 [a]	0.41 ± 0.12 [a]
	$BC_3CP_{7.5}$	0.05 ± 0.00 [a]	0.23 ± 0.08 [bc]	1.66 ± 0.16 [ab]	0.17 ± 0.12 [a]	0.26 ± 0.08 [a]

Table A7. *Cont.*

Heavy Metal	Treatments	Flesh	Skin	Root	Stem	Leaves
Pb	BC_0CP_0	0.03 ± 0.01 [a]	2.32 ± 0.01 [a]	38.74 ± 18.16 [ab]	0.60 ± 0.32 [a]	2.55 ± 0.19 [a]
	BC_1CP_0	0.04 ± 0.02 [a]	2.29 ± 2.25 [a]	41.72 ± 13.35 [ab]	1.16 ± 0.72 [a]	2.51 ± 1.09 [a]
	BC_3CP_0	0.04 ± 0.01 [a]	0.58 ± 0.21 [a]	29.00 ± 14.60 [b]	0.66 ± 0.97 [a]	5.61 ± 4.08 [a]
	$BC_0CP_{7.5}$	0.03 ± 0.02 [a]	1.60 ± 0.17 [a]	18.32 ± 6.92 [b]	0.60 ± 0.06 [a]	1.35 ± 1.18 [a]
	$BC_1CP_{7.5}$	0.03 ± 0.01 [a]	2.67 ± 0.78 [a]	59.13 ± 21.55 [a]	0.47 ± 0.10 [a]	9.37 ± 8.68 [a]
	$BC_3CP_{7.5}$	0.04 ± 0.02 [a]	2.56 ± 2.44 [a]	25.60 ± 17.98 [b]	0.80 ± 0.30 [a]	2.50 ± 2.21 [a]
Fe	BC_0CP_0	26.25 ± 1.37 [a]	134.72 ± 87.14 [a]	1021.98 ± 383.32 [a]	69.18 ± 24.81 [a]	231.93 ± 54.16 [a]
	BC_1CP_0	19.1 ± 5.28 [ab]	83.02 ± 2.23 [a]	565.36 ± 87.35 [b]	55.41 ± 40.91 [a]	167.44 ± 23.92 [a]
	BC_3CP_0	19.1 ± 3.85 [ab]	67.17 ± 34.18 [a]	580.17 ± 143.41 [b]	28.83 ± 9.04 [a]	166.36 ± 40.59 [a]
	$BC_0CP_{7.5}$	21.03 ± 6.6 [ab]	111.76 ± 67.2 [a]	602.66 ± 101.02 [b]	68.00 ± 32.42 [a]	170.29 ± 38.47 [a]
	$BC_1CP_{7.5}$	23.55 ± 3.9 [ab]	70.37 ± 5.19 [a]	963.56 ± 44.25 [a]	31.58 ± 6.52 [a]	195.26 ± 60.15 [a]
	$BC_3CP_{7.5}$	18.42 ± 3.02 [b]	42.70 ± 15.68 [a]	529.24 ± 153.27 [b]	57.32 ± 22.98 [a]	166.00 ± 63.28 [a]

[a–c] Within year, different letters in the same column indicate a significant difference ($p \leq 0.05$).

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