Chapter 15

Leachability and Vegetable Absorption of Heavy Metals from Sewage Sludge Biochar

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Additional information is available at the end of the chapter

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1. Introduction

Management of industrial wastes has been one of the most challenging problems in most urban municipalities due to increasing waste volume with limited disposal areas, and energy-consuming and high-cost treatment processes for disposal. In Japan, although the total volume of the industrial waste generated has been relatively constant since 1990 being approximately 400 million tons per year, remaining capacity of the final disposal for the industrial waste has decreased by approximately 20% since 1994, reaching to 172 million m^3 in 2007 (Ministry of the Environment Government of Japan, 2011). This disposal capacity is predicted to be filled in the average of 8.5 years for Japan, and 3.6 years for Tokyo Metropolitan areas. Due mainly to high cost of treatment for proper disposal, illegal dumping of the industrial waste has been a new problem despite of severe regulation and monitoring of affected areas. The number and total volume of unsolved cases of illegal dumping and improper disposal of the waste were 2,610 and 1.78 million tons, respectively, in 2010 (Ministry of the Environment Government of Japan, 2011).

Sewage sludge is one of the most produced industrial wastes and comprised approximately 20% (77.2 million tons) of the total volume of industrial wastes generated across Japan in 2010 (Ministry of the Environment Government of Japan, 2011). However, the volume of its final disposal was insignificant (0.37 million tons) since the majority of sewage sludge were reclaimed and/or treated by intermediate processing such as thickening, dewatering, anaerobic digestion, composting, incineration, carbonization, and melting. On the dry solid basis, 78% of the total volume of sewage sludge (1.72 million tons) was recycled in beneficial applications mainly for construction materials (1.39 million tons), energy production (0.02 million tons), and application in agriculture and horticulture as alternative fertilizers and/or soil conditioner (0.31 million tons). Due to new technology and diversification of sewage sludge recycling techniques, further recycling avenues are expected particularly for production of energy, agriculture, forestry, livestock, and fisheries in the future.

Pyrolysis process of sewage sludge is one of the useful approaches for sewage sludge recycling, and its product called sewage sludge biochar (SSB) can be used as supplemental or alternative material to coal for thermal power plants. Some municipalities in Japan have initiated to use SSB as a part of thermal sources for energy production. In Tokyo, since 2007, 8,700 tons of SSB have been produced per year from 99,000 tons of sewage sludge and mixed with coal for energy plant to contribute approximately 1% of the total calorific value by the plant. The SSB produced is pyrolysed at 500°C for one hour and generates 2,000 kcal kg^{-1} of heat calorie, which is equivalent to one third of that of coal. Aichi Prefecture started a similar project as Tokyo in 2012, and uses 2,700 tons of SSB pyrolysed at 500°C from 33,000 tons of sewage sludge every year to generate 4.6 million kWh of energy, which is capable of providing electricity equivalent to annual usages of typical 1,270 households in the area.

Sewage sludge biochar can be also used for supplemental or alternative fertilizer material for crop production. Different feedstock properties and pyrolysis temperatures, however, yield SSB with different physicochemical properties, thus exhibit different degrees of effect when SSB is applied to soil as soil amendments or fertilizers for improving crop production or soil properties (Chan & Xu, 2009). An SSB produced at 800°C in Japan contained moderate amounts of macronutrients for crop production, among which P was relatively high (78.9 g P kg^{-1}), and relatively high amounts of heavy metals (1,100 mg Cu kg^{-1}, 1,630 mg Zn kg^{-1}, 4 mg Cd kg^{-1}, 126 mg Ni kg^{-1}) which were within the limits legislated in Japan (Kawano et al., 2012). Effects of SSB application to soils up to 40% by weight on the growth of Begonia (*Begonia semperflorens*) differed depending on the soil type and were more positively pronounced in soils more infertile such as sand-dune and yellow soils. A wastewater sludge biochar pyrolysed at 550°C in Australia was applied at a rate of 10 t ha^{-1} and improved the production of cherry tomatoes (*Lycopersicon esculentum*) by 64% above the control without SSB application (Hossain et al., 2010). Some heavy metals such as Cd, Cu, and Zn were taken up more by the plant with SSB application (0.04, 6.2, and 22 mg kg^{-1}, respectively) compared with the control, however the plant uptake of all 16 metals and trace elements measured in the SSB itself were below the Australian maximum permitted concentrations for food products. As SSB pyrolysis temperature increased from 300°C to 700°C, while biochar yield, fixed C, volatile matter, total N, and inorganic N contents decreased, pH values, ash, total P, available (Colwell) P, Ca, Mg, Fe, S, Zn, Cd contents increased (Hossain et al., 2011). The total concentration of heavy metals such as Cd, Cr, Ni, and Pb tends to be enriched in the SSB, but the bioavailability (e.g., DTPA-extractable) of many of these trace elements appears to be reduced during pyrolysis process, compared with those in the raw feedstock (Hossain et al., 2011; Méndez et al., 2012). The variability of the micronutrient concentrations in biochar is due to its volatility and pyrolysis temperature effects on both composition and chemical structure of the biochar (Chan and Xu, 2009).

Agronomic effects of SSB application to soils, therefore, widely vary depending on physicochemical properties of the sewage sludge, pyrolysis temperature, and soil properties, which need to be further clarified including the heavy metal dynamics in order for the SSB application to be broadly accepted in agricultural and horticultural practices. Therefore, objectives of this study were to 1) investigate the leachability of heavy metals, particularly Cu, Zn, and Cd from SSB as applied to soil with varying rates, and 2) evaluate the effect of SSB application to soil on plants' growth and absorption of the heavy metals, using SSB produced at two different pyrolysis temperatures.

2. Materials and methods

2.1. Soil and biochar

A soil used in this study was a forest Andisol collected from a mulberry plantation forest in Hachioji, Tokyo, Japan (35.692, 139.316) on Apr. 29, 2011. Surface 15-cm soils were sampled, dried at 45°C overnight, sieved through 2 mm, and used for physicochemical analyses and a pot study.

Sewage sludge biochars were produced in commercial plants at high (approximately 800°C; SSB-H) and low (approximately 300°C; SSB-L) temperatures, crashed by hummer, and sieved through 2-mm sieve for chemical analyses, and homogenized between 2 and 5 mm in size for the pot study.

2.2. Pot study

A pot study was performed on campus of Soka University, Tokyo, Japan. Japanese mustard spinach (*Brassica rapa*) and common bean (*Phaseolus vulgaris*) were planted in 1.3 L planting pots in which the soil and SSB were mixed at different rates. Experimental design was a completely randomized block design with triplicate, two different plants, and four different application rates for each SSB: 0%, 25%, 50%, and 75% (v/v) for SSB-H, and 0%, 5%, 15%, and 25% (v/v) for SSB-L. Each pot received respective amounts of ammonium nitrate, superphosphate, and potassium chloride before planting based on fertilizer application rates recommended for the plants by Tokyo Prefecture: 140-52-100 kg N-P-K ha^{-1} for spinach and 80-39-66 kg N-P-K ha^{-1} for bean. Each plant was sowed on Sep. 23, 2011, and thinned to 4 spinach individuals and 2 bean individuals per pot 2 weeks later. The plants were grown outside and the pots were covered by plastic sheet only when rainfall events occurred. Water was applied periodically to keep 50% of water holding capacity of the soil-SSB mix. Spinach and bean were harvested 46 and 66 days after sowing on Nov. 8 and Nov. 28, 2011, respectively. Throughout the experiment, the daily mean temperature fluctuated between 16°C and 22°C, and the daily rainfall more than 20 mm occurred 5 times on Oct. 5, 15, 22, Nov, 11, and 19, 2011.

After harvest, the plants were divided into shoot, root, and bean sheath (only for common bean), and dried at 70°C overnight. The soil and SSB in the pot were separated using 2-mm sieve, and separately dried at 45°C overnight.

2.3. Soil, biochar, plant analyses

Dry weight (DW) of each part of the plants was determined after drying at 70°C overnight.

The soil, SSBs, and plant tissues after the pot study were ground to pass through 150 μm in size and digested for total elemental analyses for heavy metals. Two grams of the soil sample was heated to 180°C with 30 mL of concentrated nitric acid in a beaker with a glass watch on a hotplate until it turned like a syrup. Then, 30 mL of a perchloric acid-nitric acid mixture (1:4) was added and heated for further 10 min. After cooling, 25 mL of hydrochloric acid (1:5) was added and heated to 130°C for 1 hr. After cooling, the content was quantitatively transferred to a 100 mL flask and filtered through a Whatman No 1 paper (Committee for Analytical Methods for Soil Environment, 1997). Two grams of the SSB sample in crucible was ashed in an electric furnace at 550°C for 8 hr, and the ash was transferred to a beaker with 5 mL of concentrated nitric acid and heated to 120°C on a hotplate for 3 hr. After cooling, 25 mL of hydrochloric acid (1:5) was added and heated at 120°C for further 60 min. After cooling, the content was quantitatively transferred to a 25 mL flask and filtered through a Whatman No 1 paper (Japan Soil Association, 2010). One gram of each of the shoot, root, and sheath plant samples was heated to 140°C with 10 mL of concentrated nitric acid in a beaker with a glass watch on a hotplate until the content is reduced to approximately 1 mL. After cooling, the content was quantitatively transferred to 25 mL flask using 1% nitric acid, and filtered through a Whatman No 1 paper (Committee for Experimental Methods for Plant Nutrition, 1990).

The heavy metals extractable by 0.1 *M* HCl are used as an indicator for environmental pollution in soils. Various chemical extractants are used for single extraction evaluation of heavy metals and may broadly be divided into 3 main classes: (i) weak replacement of ion salts ($MgCl_2$, $CaCl_2$, NH_4CO_3), (ii) dilute solutions of either weak acid (acetic acid) or strong acids (HCl, HNO_3), and (iii) chelating agents (DTPA, EDPA) (Kashem et al. 2007). The unbuffered ion salt solutions are simple procedure to extract bioavailable metals, while a use of 0.1 *M* HCl solution may reflect bioavailability of metals (CSTPA, 1980). Dried 7.0 g of soil samples (< 2 mm) was weighed to a 50 mL centrifuge tube and 35 mL of 0.1 *M* HCl was added. The tube was shaken horizontally for 1 hr at 160 stroke min^{-1}, centrifuged at 5,000 rpm, and the supernatant was filtered through a Whatman No 1 paper (Committee for Analytical Methods for Soil Environment, 1997).

Prior to analytical determination, all filtrates were further filtered through a 0.45 μm membrane. Total and extractable concentrations of Cu, Zn, and Cd in the soil, SSBs, and plant samples were determined using ICP (ICPS-7000 ver. 2.1, Shimazu).

2.4. Statistical analyses

Significant differences of the total and extractable concentrations of Cu, Zn, and Cd in the soil, SSBs, and plant samples among different SSB application rates for each SSB type and each plant were tested by ANOVA using STATISTICA 6.1 (StatSoft Inc., Tulsa, Okalahoma, USA). Unless otherwise stated, the differences were significant at $p \leq 0.05$ level.

3. Results

3.1. Soil and biochar properties

The Andisol used in this study had an almost neutral pH (H_2O) of 7.1 and relatively average TC and TN concentrations (Table 1). The total heavy metal concentrations in the soil were 25 mg Cu kg^{-1}, 43 mg Zn kg^{-1}, and 4.9 mg Cd kg^{-1}. The SSB used in this study had slightly acidic pH levels of 6.6 (SSB-H) and 5.6 (SSB-L). The total Cd concentrations were similar for both SSB types ranging 1.4–1.5 mg kg^{-1}, while the total Cu and Zn concentrations in the

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SSB-H were 5 and 1.7 times greater than those in the SSB-L, respectively. The dilute acid (0.1 *M* HCl)-extractable heavy metals varied among elements and SSB types; Cu concentration in SSB-H was 34 times greater than that in SSB-L, while Cd in SSB-H was 5 times less than that in SSB-L.

	pH†	Total C	Total N	Total Cu	Total Zn	Total Cd	HCl Cu‡	HCl Zn‡	HCl Cd‡
		g kg^{-1}		mg kg^{-1}					
Andisol	7.1	45.1	2.8	25	43	4.9	0.23	2.06	0.024
SSB-H§	6.6	532.2	34.1	346	455	1.4	19.2	14.1	0.022
SSB-L§	5.6	528.4	54.8	69	273	1.5	0.56	27.3	0.12

† 1:2.5 soil:solution with H_2O and 1:100 SSB:solution with hot H_2O

‡ 0.1 *M* HCl-extractable

§ SSB pyrolysed at high temperature (800°C; SSB-H) and low temperature (300°C; SSB-L)

Table 1. Basic properties of the soil (Andisol) and sewage sludge biochar (SSB) used in this study.

3.2 Dry weight of the plants

Seeds of both plants with all treatments germinated 100% except for those of the bean with SSB-L 25% treatment being 66% of the germination rate.

The average DW of individual spinach shoot showed a significant decrease with increasing application rates of both SSB-H and SSB-L, respectively (Fig. 1a). The highest DW was 1.1 and 1.4 g with SSB-H 0% and SSB-L 5% treatment, respectively. The average DW of the bean shoot did not show significant differences among the SSB-H treatment, but a significant increase with SSB-L 5% and 15% compared with that of control.

The average DW of the spinach root showed a significant decrease with increasing application rate of SSB-H, but not among the SSB-L treatment except for SSB-L 25% showing the lowest DW among the treatment (Fig. 1b). The average DW of the bean root showed a significant decrease with the increasing SSB-H application rate, and a significant increase only with SSB-L 15% among the SSB-L treatment.

The average DW of the bean sheath was not significantly affected by the SSB application, ranging from 0.04 and 0.18 g among the SSB-H treatment, and 0.04 g for SSB-L 5% rate (the bean did not bear the sheath with SSB-L 15% and 25% rates; Table 2).

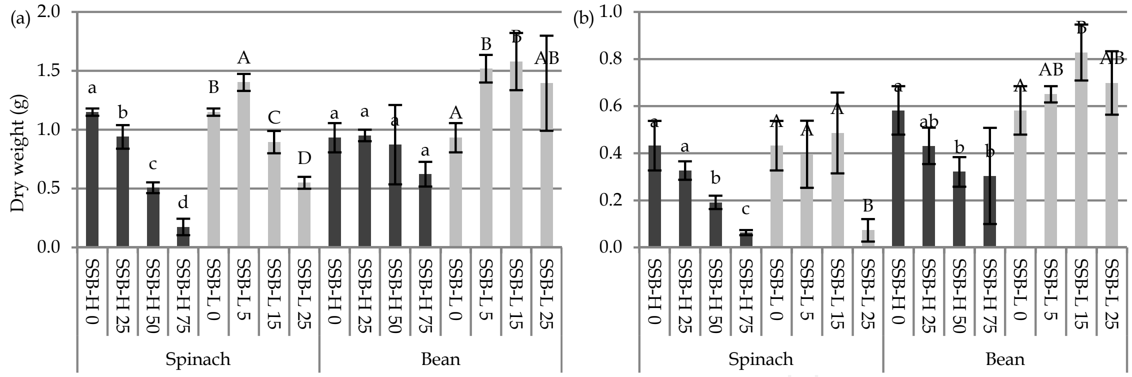

Figure 1. Dry weight of (a) shoot and (b) root parts of Japanese mustard spinach and common bean with different application rates of sewage sludge biochar pyrolysed at high (SSB-H) and low (SSB-L) temperatures. Different letters denote significant differences by Fisher test (p<0.05) among different application rates for each plant and SSB, respectively.

	DW	Cu	Zn	Cd		DW	Cu	Zn	Cd
	g	mg kg^{-1}				g	mg kg^{-1}		
SSB-H 0	0.07ab	5.37a	3.04a	0.58a	SSB-L 0	0.07A	5.37A	3.04A	0.58A
SSB-H 25	0.17ab	1.99a	2.62a	0.28b	SSB-L 5	0.04A	10.75A	5.00A	1.46A
SSB-H 50	0.18a	1.87a	3.36a	0.26b	SSB-L 15	na	na	na	na
SSB-H 75	0.04b	5.77a	3.43a	0.73a	SSB-L 25	na	na	na	na

Table 2. Dry weight (DW), Cu, Zn, and Cd concentrations in the common bean sheath with different application rates of sewage sludge biochar pyrolysed at high (SSB-H) and low (SSB-L) temperatures. Different letters denote significant differences by Fisher test (p<0.05) among different application rates for each SSB and plant, respectively. na denotes non-applicable.

3.3. Total heavy metal concentrations in the plants

Copper concentrations in the spinach shoot significantly increased with both SSB treatments over the control, respectively, while, although not significantly different, those in the bean shoot were lower with both SSB treatments compared with the control, respectively (Fig. 2a). Zinc concentrations in the spinach shoot significantly increased with both SSB treatments over the control, respectively, except for SSB-L 5% rate (Fig. 2b). On the other hand, Zn in the bean shoot was not significantly affected by both SSB treatments, except for SSB-L 5% being significantly lower than the control. The shoot part of each of both plants contained significantly greater Cd concentrations with both SSB treatments over the control, respectively (Fig. 2c).

The concentrations in the plant root were generally greater than those in the shoot for all heavy metals investigated regardless of the plant, SSB type and application rate. The Cu concentration in the spinach root was greatest with SSB-H 25% rate and SSB-L 15% rate among SSB-H and SSB-L treatments, respectively, while Cu in the bean root was greatest with SSB-H 50% rate and SSB-L 25%, among each SSB treatment, respectively (Fig. 2d). The Zn concentrations in the spinach root with SSB-H 25% and 50% rates were significantly greater than that of the control, and although not significant, those with the SSB-L treatment were greater than that of the control (Fig. 2e). The bean root absorbed significantly greater Zn with SSB-H 50% and 75% rates, and not significantly but greater Zn with SSB-L 15% and 25% rates, compared with that of the control, respectively. Cadmium in the spinach root was significantly higher with SSB-H 75% rate than those at other rates, but Cd with the SSB-L treatment was lower than that of the control (Fig. 2f). The Cu in the bean root was significantly lower with SSB-H 75% rate and higher with SSB-L 0% rate compared to other rates, respectively.

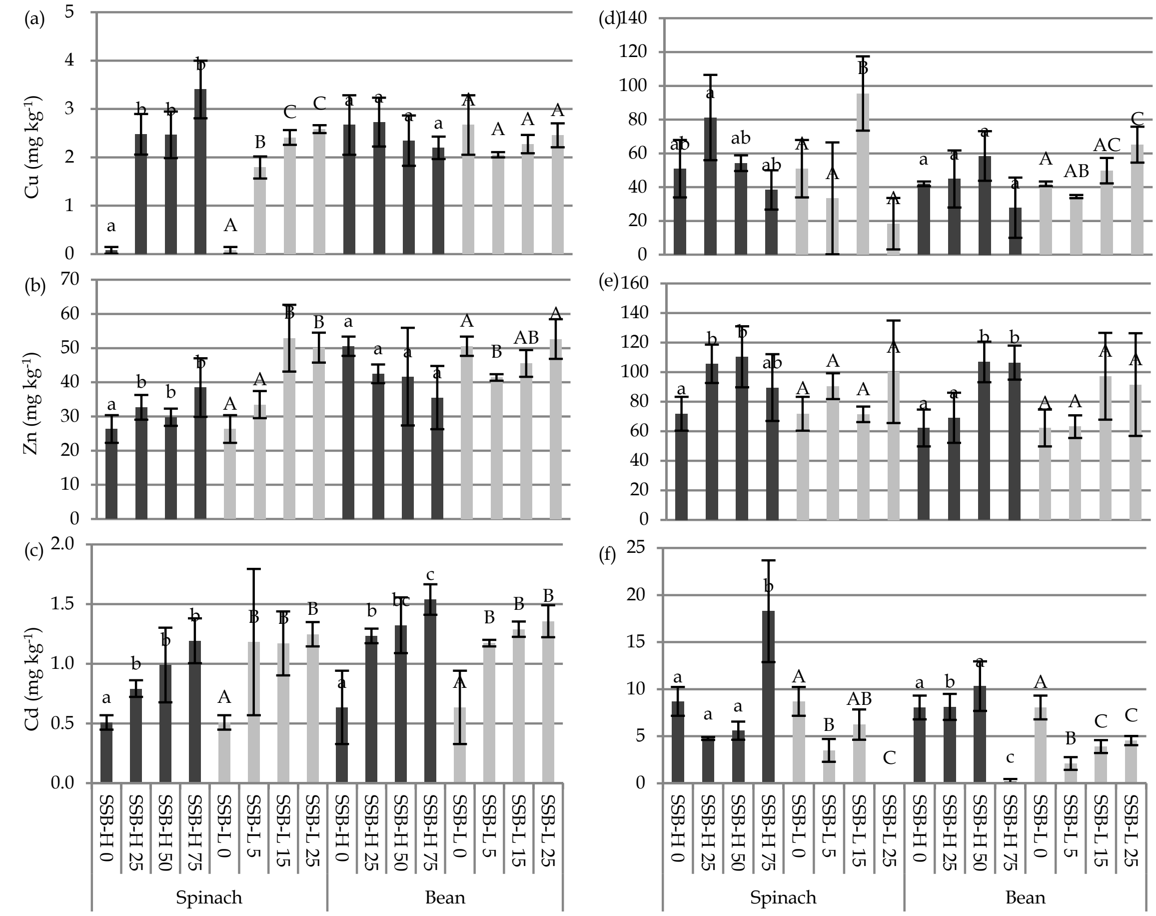

Figure 2. Total concentrations of (a) Cu, (b) Zn, and (c) Cd in the shoot and (d) Cu, (e) Zn, and (f) Cd in the root of Japanese mustard spinach and common bean with different application rates of sewage sludge biochar pyrolysed at high (SSB-H) and low (SSB-L) temperatures. Different letters denote significant differences by Fisher test (p<0.05) among different application rates for each plant and SSB, respectively.

Any of Cu, Zn, and Cd in the sheath was not significantly affected by either application of SSB-H or SSB-L compared with that of the control, respectively, except for Cd with SSB-H 25% and 50% rates being significantly higher than that of the control (Table 2).

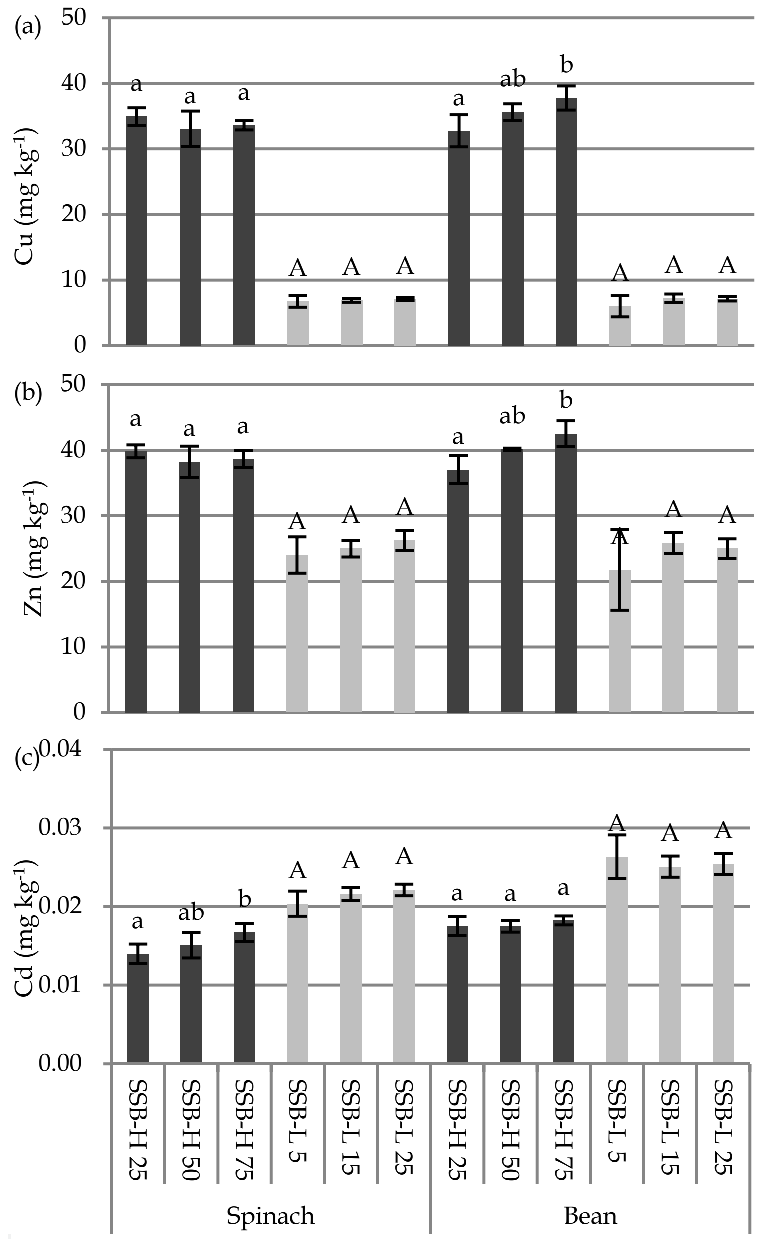

Figure 3. Total concentrations of (a) Cu, (b) Zn, and (c) Cd in the biochar after the pot study with different application rates of sewage sludge biochar pyrolysed at high (SSB-H) and low (SSB-L) temperatures. Different letters denote significant differences by Fisher test (p<0.05) among different application rates for each plant and SSB, respectively.

3.4. Total heavy metal concentrations in the biochar after the pot study

The total Cu concentration in the SSB-H after the pot study was not significantly affected for the spinach but significantly increased with SSB-H 75% rate for the bean (Fig. 3a). The total Cu concentrations in the SSB-L were not significantly affected by the application rate for both plants. After harvest of the spinach the total Zn in the biochar was not affected by the application rate for both SSBs, but at the bean's harvest only SSB-H 75% rate caused significantly higher total Zn among the SSB-H treatment (Fig. 3b). The total Cd in the biochar did not significantly change among each of the SSB rates and plants, respectively, except for that with SSB-H 75% rate with the spinach being significantly greater than other SSB-H rates (Fig. 3c).

3.5. Total heavy metal concentrations in the soil after the pot study

The total Cu concentration in the soil after the pot study was significantly increased only with SSB-H 75% rate among the SSB-H treatment for both plants, respectively, but not affected among the SSB-L treatment for both plants (Fig. 4a). The total Zn in the soil tended to increase with the SSB-H application rate and was significantly greater with SSB-H 75% rate compared with those with other rates (Fig. 4b). The total Zn in the soil was not significantly different among the SSB-L treatments for both plants. The total Cd in the soil was significantly increased with SSB-H 25% and 50% rates for the spinach, but not affected for the bean (Fig. 4c). The total Cd in the soil with the SSB-L treatment significantly increased compared with that of the control for both plants, respectively.

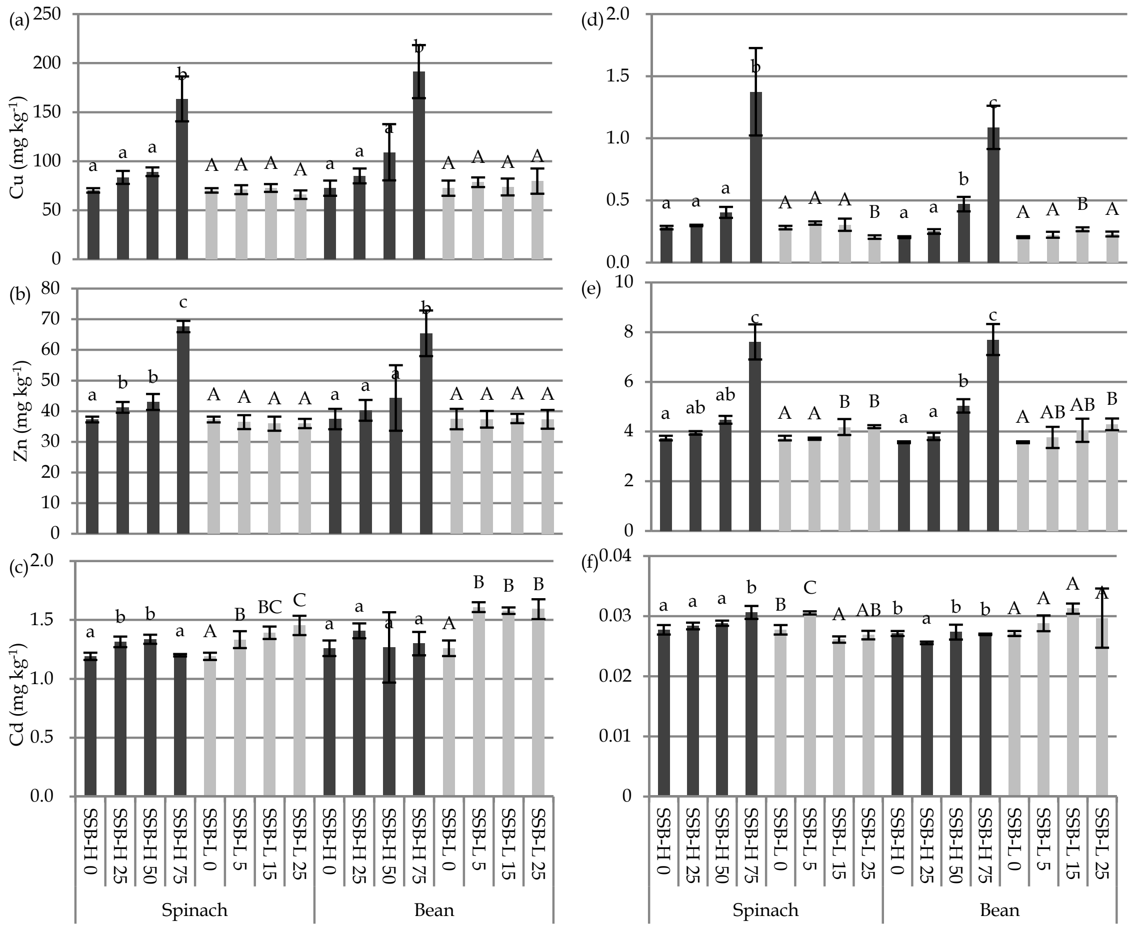

Figure 4. Total concentrations of (a) Cu, (b) Zn, and (c) Cd and dilute acid (0.1*M* HCl)- extractable (d) Cu, (e) Zn, and (f) Cd in the soil after the pot study with different application rates of sewage sludge biochar pyrolysed at high (SSB-H) and low (SSB-L) temperatures. Different letters denote significant differences by Fisher test (p<0.05) among different application rates for each plant and SSB, respectively.

3.6. Acid-extractable heavy metal concentrations in the soil after the pot study

The dilute acid (0.1 *M* HCl)-extractable Cu in the soil after the pot study tended to increase with increasing SSB-H application rate for both plants, respectively, and those with 75% for spinach, and 50% and 75% for bean were significantly greater than those with lower rates, respectively (Fig. 4d). The HCl-Cu with SSB-L 25% for spinach and SSB-L 15% for bean was significantly lower and higher, respectively, than those with other rates. Similarly, the HCl-Zn with SSB-H 75% rate for spinach and SSB-H 50% and 75% rates for bean were significantly greater than those with other rates, respectively (Fig. 4e). The HCl-Zn with SSB-L 15% and 25% were significantly greater than those with other rates for spinach, and that with SSB-L 25% rate was significantly greater than those with other rates for bean. The HCl-Cd with SSB-H 75% rate was significantly higher than those with other rates for spinach, and that with SSB-H 25% rate was significantly lower than those with other rates for bean (Fig. 4f). The HCl-Cd with SSB-L 5% was greater compared with those with other rates for spinach, but there were no significant differences among the SSB-L treatment for bean.

4. Results and discussion

4.1. Heavy metal concentrations in the soil and biochar

It appears that the Andisol used in this study contained less but comparable total Cu and Zn, and greater total Cd concentrations compared with the concentration range in similar soils of Japan. The concentrations of Andisols sampled in surrounded subareas of Tokyo ranged from 97 and 140 with the average of 118 mg Cu kg^{-1}, from 121 and 175 with the average of 143 mg Zn kg^{-1}, and from 0.37 and 0.55 with the average of 0.44 mg Cd kg^{-1} (Terashima et al., 2004). Some heavy metals including Cu, Zn, and Cd have tendency of being retained thus accumulated in soils given being relatively immobile after weathering in the soil (Terashima et al., 2004). High concentrations of some heavy metals including Cd, Hg, Pb, and Sb were observed because of possible artificial interventions especially in suburb areas of Tokyo (Terashima et al., 2007). In fact, the area where the Andisol used in this study was sampled was a former forest converted to a plantation area for mulberry (*Morus alba* L.) tree. The conversion and maintenance processes of the plantation could have involved some artificial interferences that might involve Cd deposition to the area.

Many properties including heavy metal concentrations in SSB widely vary primarily depending on those contained in the feedstock (Chan & Xu, 2009). An SSB pyrolysed at 800°C from sewage sludge in Kyoto, Japan contained 1,100 mg Cu kg^{-1}, 1,630 mg Zn kg^{-1}, 4 mg Cd kg^{-1} (Kawano et al., 2012), while one pyrolysed at 500°C using sewage sludge in Madrid, Spain contained 222 mg Cu kg^{-1}, 1,250 mg Zn kg^{-1}, 1.79 mg Cd kg^{-1} (Paz-Ferreiro et al., 2012). It seems that both SSB used in this study fall in the low end of concentration ranges for Cu, Zn, and Cd in the SSB found in the literature. Particularly, Zn concentrations in both SSBs were exceptionally lower than those in the literature. The heavy metal concentration in the SSB appears to accumulate as the pyrolysis temperature increases (Hossain et al., 2011), to which the SSB used in this study followed a similar pattern.

4.2. Effect of biochar on plant growth

The DW of spinach shoot and root and bean root significantly decreased with increasing rates of SSB-H due mainly to a lack of soil volume in the pot. In fact, chlorosis due to N deficiency was observed with the SSB-H treatment and more pronounced on leaves of both plants with higher SSB-H rates. Although the plant was fertilized, it appeared that the lack of soil volume in the pot with high SSB-H rates limited plant root growth thus the plant growth. In addition, although the concentration was not measured in soil or plants, both plants with the SSB-L treatment showed a leave curvature due possibly to excess uptake of boron. When SSB-L was applied, however, the shoot of both plants grew more than that of the control and their DW peaked at 5% rate for spinach and 15% for bean. A similar trend was observed when a begonia (*Begonia semperflorens*) was grown on an Andisol mixed with SSB pyrolysed at 800ºC resulting in the DW peak with 25% rate (v/v) (Kawano et al., 2012). In Kawano's study, the effect of SSB application on the plant growth was most pronounced on a most infertile sandy Entisol (Typic Udipsamments) among tested soils with the highest SSB application. It appears that the positive effect of SSB application to soil on the plant may be more prominent in soils which are less favorable for plant growth (Kawano et al., 2012). On the other hand, when an SSB pyrolysed at 700ºC was applied to a volcanic ash soil from Kanto area, Japan with 0% (control), 30%, 50%, and 100% (v/v) application rates to grow common bean, the DW at harvest with each treatment was in the order of control<100%<30%<50% (2.2, 3.6, 4.0 times of control, respectively), and rhizobia with all SSB treatments developed more than that with control (Teranuma & Mori, 2002). It appears that the optimum application rates of SSB for maximum plant growth widely depend on varying properties of soil, SSB, and plant, on which requires further investigations.

4.3. Plant absorption of heavy metal

Some heavy metals such as Zn, Cu, and Ni are important for proper functioning of biological systems and deficiency or excess can lead to a number of disorders (Ward, 1995), while others such as Cd are dangerous pollutant due to their high toxicity to plants and inhibit growth at high absorption (Liu et al., 2006). The range of heavy metal concentrations absorbed in both shoot and root of the plants was in the order of Cd<Cu<Zn, respectively, in this study. The same order of the concentration range of heavy metals was observed in various vegetable crops including similar plants used in this study as spinach (*Amaranthus caudatus*), lettuce (*Lactuca sative*), and peas (*Pisum sativum* L.) (Uwah et al, 2011; Singh et al., 2012). The concentrations of Cu, Zn, and Cd in healthy plants can range 4–15, 25–125, and 0.2–0.8 mg kg^{-1}, respectively (National Institute for Agro-Environmental Sciences, 1977). The total Cu and Zn concentrations in the shoot of both plants in this study may have fallen in safe concentration ranges, respectively, whereas the total Cd may have been in excess absorption range which may have caused inhibition of the plant growth. In fact, the DW of the shoot of the plants showed inverse relationships with the total concentrations of the heavy metals absorbed in the plants' shoot, except for the bean DW under the SSB-L treatment with the total Cd (Table 3). The inhibitive effect of heavy metal absorption on the plant growth, judged by the slope of the correlation equation, was in the order of Zn<Cu<Cd for both plants and both SSB types, respectively.

Particularly, the correlation coefficient was highest for Cd among the heavy metals with the SSB-H treatment for the spinach (0.719). A similar trend was observed when heavy metals' effectiveness in producing oxidative damage on spinach, assessed by the manifestation of external visual toxicity effects, was in the order of Zn<Cu<Cd (Pandey et al., 2009). Interestingly, however, the bean shoot showed Cd tolerance to some degree with the SSB-L treatment in this study (its correlation coefficient was positive).

Plant/SSB	Equations	Coefficients
Spinach/SSB-H	(DW) = –0.00097*(Cu) + 0.0048	0.651
	(DW) = –0.00015*(Zn) + 0.0074	0.345
	(DW) = –0.00443*(Cd) + 0.0066	0.719
Spinach/SSB-L	(DW) = –0.00076*(Cu) + 0.0052	0.281
	(DW) = –0.00008*(Zn) + 0.0070	0.422
	(DW) = –0.00129*(Cd) + 0.0051	0.121
Bean/SSB-H	(DW) = –0.00008*(Cu) + 0.0019	0.007
	(DW) = –0.00001*(Zn) + 0.0021	0.038
	(DW) = –0.00022*(Cd) + 0.0020	0.044
Bean/SSB-L	(DW) = –0.00053*(Cu) + 0.0041	0.082
	(DW) = –0.00006*(Zn) + 0.0054	0.219
	(DW) = 0.00151*(Cd) + 0.0010	0.537

Table 3. Correlation equations and coefficients between the dry weight (DW) and total concentrations of Cu, Zn, and Cd absorbed in the shoot of the plants.

Overall concentrations of Cu, Zn, and Cd in the root were greater than those in the shoot of the plants probably because of root's chelating exudates to solubilize heavy metals in the rhizosphere (Inaba & Takenaka, 2000) and rapid absorption by the root and slow translocation to shoot (Nada et al., 2007). Accumulation of heavy metals (Cu, Zn, and Cd) in spinach after exposure to 500 μM supply of the metals was greater in the root than in the leaf and stem at the end of experiment (Pandey et al., 2009). The rate of heavy metal absorption by the plant can be affected by many factors of both soil and plant such as soil pH, plant age, plant species, and nature of soil and climate (Alloway & Ayres, 1997; Uwah, 2009). Although not verified, the application of acidic SSBs used in this study may have decreased the neutral pH of the soil during the pot study, which may have enhanced plant absorption of especially Zn and Cd, as commonly observed irrespective of the vegetable crops and soil types (Kuo et al., 1985; Xue & Harrison, 1991). The effects of SSB application on soil properties, heavy metal bioavailability, and plant growth, therefore, need to be further evaluated for the range of different soils and plants, and over time because heavy metal bioavailability may increase over time in soil (Schauer et al., 1980).

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4.4. Heavy metal leachability from biochar

The total concentrations of Cu, Zn, and Cd in SSB after the pot study did not greatly vary among the application rates within the same SSB type and plant, respectively, and 89–91%, 90–92%, and 98–99% of the original concentrations of Cu, Zn, and Cd were lost from the SSB during the pot study, respectively, regardless of the SSB type, application rate, and plant. While there are numerous studies that deal with sorption capacity of biochars for heavy metals when applied to soil in light of phytoremediation perspective (Cao et al., 2009; Namgay et al., 2010; Uchimiya et al., 2011), studies regarding on leachability (through desorption or dissolution) of heavy metals from biochar and their bioavailability are virtually nonexistent. The heavy metals, however, are known to be desorbed by naturally occurring organic acids such as citric, oxalic, acetic, and lactic acids (Nascimento, 2006; Marchi, 2009) and dissolved organic carbon (Antoniadis & Alloway, 2002) from soils amended with sewage sludge. Regardless of equilibrium amounts of Cd adsorbed in an Andisol, more than 80% of Cd was desorbed with one time extraction with citric acid if its concentration was more than 0.1 *M*, and more than 90% was recovered if five soil pore volumes of 0.1 *M* citric acid were continuously run through the Cd-contaminated soil (Abe et al., 2004). An increase of dissolved organic matter in soil by the application of digested dewatered sludge significantly reduced the sorption of Cu on both acidic sandy loam and calcareous clay loam (Zhou & Wong, 2001). The application of SSBs in this study may have increased dissolved organic carbon given the SSBs being acidic, which may have increased Cu desorption (extractability) thus also bioavailability. The heavy metals in the SSB used in this study may have leached due to functions of various interactions between soil and plant roots. Further studies are needed to clarify leachability and bioavailability of heavy metals from biochars whose feedstock contain significant amounts of heavy metals in order to elucidate heavy metal dynamics in soil upon the application of such biochars.

4.5. Heavy metal accumulation and availability in soil

The total concentrations of Cu and Zn in the soil after the pot study, regardless of the treatment, were greater and almost equal compared with those of the original soil (25 and 43 mg kg^{-1}, respectively), while both concentrations significantly increased when SSB-H was applied at 75% rate for both plants. On the other hand, the overall concentrations of the total Cd were smaller after the pot study compared with that at pre-plant condition (4.9 mg kg^{-1}); however those with the SSB-L treatment increased with increasing application rate for both plants. Transfer factors (TF) of heavy metal, as calculated as the ratio of the concentration of heavy metal absorbed in a plant to the concentration of heavy metal in soil, can quantify the relative differences in bioavailability of heavy metals to vegetables or to identify the efficiency of a vegetable species to accumulate a heavy metal (Uwah et al., 2011). The TF values in this study, calculated based on the sum of heavy metal concentrations of the shoot and root as the plant concentration and the sum of heavy metal concentrations in the soil and SSB as the soil concentration, were 0.77, 0.83, and 1.37 for spinach, and 0.69, 0.91, and 1.19 for bean for Cu, Zn, and Cd, respectively, regardless of the SSB application rate. These TF values may explain why Cu appeared to have been accumulated in the soil (TF less than 1 and lowest among the 3 metals for both plants), Zn seemed to have had no changes before and after the pot study

(TF close to 1), and Cd appeared to have been accumulated more in the plant than in the soil (TF more than 1). The TF values widely vary depending on properties of soils and plants, however, those calculated in this study may be comparable with those found by Uwah et al. (2011), which were 0.25–0.95, 0.38–0.55, and 0.42–2.75 for Cu, Zn, and Cd, respectively, for spinach and lettuce grown on tropical soils in Nigeria. Further studies are needed to elucidate heavy metal accumulation in soil and selective absorption by plants with the SSB application.

The heavy metal concentrations extractable by 0.1 *M* HCl acid solution in the soil after the pot study followed similar patterns as the total concentrations in the soil. The Cu and Zn concentrations significantly increased only when SSB-H was applied at 75% rate for both plants, while the Cd concentrations did not show noteworthy differences among the treatment. However, the percentage of the concentration of the acid-extractable Cu, Zn, and Cd to the total concentration (acid solution extractability) was 0.3–0.8%, 9.4–11.8%, and 1.8–2.6%, respectively. When 4 contaminated and 4 non-contaminated soils from a northern part of Japan were extracted for heavy metals using 0.1 *M* HCl, the extractability ranged 12% and 27–33% for Cu, 9% and 12–31% for Zn, and 33% and 73–92% for Cd in the contaminated and non-contaminated soils, respectively (Kashem et al., 2007). Although the extractability of heavy metals from soil by the dilute acid may vary depending on soil type, heavy metal, contamination degrees, and so on, 0.1 *M* HCl extractant may be the best choice for assessment of mobility or bioavailability of heavy metals (Kashem et al., 2007).

The environmental threshold concentrations in soils are 125 mg Cu kg^{-1}, 125 mg Zn kg^{-1}, and 0.01 mg Cd L^{-1} as 0.1 *M* HCl extractable heavy metals, set by the Japanese Environmental Ministry. It seems that neither of SSB types within the application rates and study duration used in this study have caused environmental threads to soils. Based on life cycle assessment analysis on different treatment processes of sewage sludge including anaerobic digestion, pyrolysis, and incineration, it was concluded that the most effective utilization of sewage sludge implied both energy and material reuse, and that the land application of digested sludge was an acceptable and good choice as long as heavy metal contents in the final cake could be minimized (Hospido et al., 2005). Therefore, long-term effects of SSB application on heavy metal dynamics among SSBs, soils, and plants are needed to be evaluated for further acceptance of SSB application in agronomic benefits.

5. Conclusions

Biochars derived from feedstock including heavy metals such as SSB need to be thoroughly evaluated for heavy metal dynamics among SSBs, soils, and plants for environmentally safe and sound application of SSB. Both SSBs used in this study contained a low end of concentration ranges of Cu, Zn, and Cd, respectively, found in the literature, and the heavy metal concentrations accumulated in the SSB as the pyrolysis temperature increased as found in the literature. Both spinach and bean plants suffered from N deficiency due mainly to a lack of soil volume with excessively high application of SSB-H, and possibly from B toxicity especially from SSB-L application. However, when SSB-L was applied, the shoot DW of plants peaked

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with 5% application rate for spinach and 15% rate for bean. Therefore, it was concluded that the optimum application rates of SSB-H and SSB-L were indeterminate (lower application rates of SSB-H need to be evaluated) and 5–15%, respectively, for the best growth of the plants in this study. The concentration ranges of the heavy metals absorbed in both plants were in the order of Cd<Cu<Zn for both shoot and root. The total Cu and Zn in the shoot may have been in safe concentration ranges, and the total Cd may have been in excess range which may have caused inhibition of the growth. In fact, the plant DW showed inverse relationships with the total concentrations of the heavy metals absorbed in the plants, and the inhibitive effect of heavy metals on the plant growth was in the order of Zn<Cu<Cd. Overall concentrations of the heavy metals in the root were greater than those in the shoot for both plants. The leachability of Cu, Zn, and Cd from SSBs was 89–91%, 90–92%, and 98–99% of the original total concentrations, respectively, during the pot study regardless of the SSB type, application rate, and plant. However, the total concentrations of Cu, Zn, and Cd in the soil after the pot study were accumulated, unaffected, and reduced, respectively, compared with those before the pot study, which could be explained by the TF of each heavy metal which were less than 1, close to 1, and more than 1, respectively. Nevertheless, the percentage of the dilute acid-extractable Cu, Zn, and Cd to the total concentrations in the soil after the pot study was 0.3–0.8%, 9.4–11.8%, and 1.8–2.6%, respectively, which were lower than the environmental threshold concentrations in Japan. However, long-term effects of SSB application on heavy metal dynamics among SSBs, soils, and plants are needed to be evaluated for further acceptance of SSB application in agronomic benefits.

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