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Effects of fine fractions of soil organic, semi-organic, and inorganic amendments on the mitigation of heavy metal(loid)s leaching and bioavailability in a post-mining area

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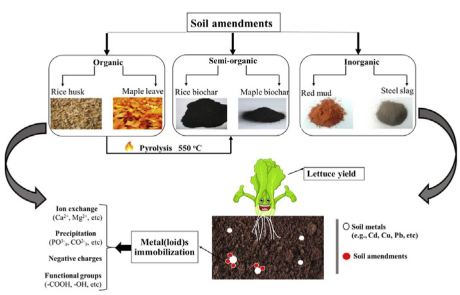
HIGHLIGHTS

- Effect of soil amendments varieties on metal(loid)s stabilization was investigated.
- Stabilization efficiency varied by amendments properties and metal(loid)s species.
- Alkaline amendments reduced the amount of easily-leachable fractions of metals.
- Biomass and biochar in soil induced plant growth, but reduced As uptake by lettuce.
- Maple biochar and steel slag showed the most stabilization efficiency for metals.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the effects of soil amendments including biomasses (rice husk, RRH and maple leaf, RML), biochar (rice husk biochar, RHB and maple leaf biochar, MLB), and industrial by-products (red mud, RM and steel slag, SS), at two application rates (0, 1, and 2% w/w) on leaching and bioavailability of heavy metal(loid)s (HMs) (As, Cd, Cu, Pb, and Zn) in the presence of an *Asteraceae* (i.e., lettuce). Physicochemical properties of the soil (i.e., pH, EC, CEC, and HMs leaching) and plants were examined before and after amending. The addition of amendments significantly ($p < 0.05$) increased soil EC (from 100 to 180 μScm^{-1}) and CEC (from 7.6 to 15 meq100 g^{-1}). Soil pH from 6.7 $\pm$ 0.05 increased about 2 units with increasing in the application rate of MLB, RM, and SS, while it decreased about 0.8 units in RML amended soil. Soil amendments reduced the easily leachable fractions (exchangeable and carbonate) of HMs in the order of MLB > SS > RM > RHB. The average concentration of Cd, Cu, Pb, and Zn in plant roots and shoots decreased >30 wt% in biochars and industrial by-products amended soils, while biomasses mitigated As uptake in lettuce. Results demonstrated that adding maple-derived biochar combined with revegetation effectively immobilized HMs in a post-mining area beside an induce in plant growth parameters.

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1. Introduction

Heavy metals (HMs) contamination in soil is becoming a major issue of concern all over the world. Mining activities are considered as one of the most influential anthropogenic activities which result in the degradation of land resources, destruction of habitats, and contamination of soil and water with HMs (Shifaw, 2018; Wei et al., 2018). Inefficient processing procedures of mining ores cause an abundance of HMs residues in mine tailings. There are many abandoned metal mines in Korea, and piles of untreated tailings are left in the vicinity of these mining sites (Kim et al., 2002; Govarthanan et al., 2013). The mine tailings are exposed to the farmlands around and lead to the mobilization and dispersion of HMs (Zhu et al., 2018). Considering the general shortage of cultivated land in Korea, the cultivation of farmland around mining sites could make a significant contribution to Korean food production, which may later cause a human health problem (Kim et al., 2002). Therefore, various physical, chemical, and biological techniques have been used to remediate HMs contaminated soils (Wang et al., 2020; Xu et al., 2020; Yang et al., 2021). Among different technologies, in-situ immobilization is generally considered a feasible technique to remediate multi-metal contaminated soils mainly because it is easy to operate and cost-effective (Derakhshan-Nejad et al., 2017; Govarthanan et al., 2014; Palansooriya et al., 2020). Many researchers have reported on the use of various soil amendments to immobilize HMs in contaminated sites, including calcareous materials, phosphates, clay minerals, and so on (Derakhshan-Nejad and Jung, 2018a; Govarthanan et al., 2015, 2018; Xu et al., 2020). Indeed, identifying appropriate chemical and biological materials as a soil amendment is a big concern because it probably alters soil properties such as alkalization, hardening, and microbiological disturbances and subsequently changing soil quality.

Biochar, a carbonaceous material produced by the pyrogenic decomposition of biomass above 250 °C with a limited oxygen content (Lehmann and Joseph, 2015), seems to be a feasible and promising solution to soil contamination (Pratiwi et al., 2016; Wang et al., 2020). Previous studies showed that appropriate feed materials for biochar production need to be selected carefully before practical application of them as soil amendments. Biochar has benefits to improve the degradation of soil and enhance crop growth and yields (Hussain et al., 2017; Oni et al., 2019). Besides, using industrial by-products such as red mud and steel slag as soil amendments showed promising results in mitigating HMs bioavailability. These Fe and Al sources' rich amendments are essential to reduce As and metals toxicity and hence facilitate plant survival (Ning et al., 2016; Hua et al., 2017).

The chemical speciation and microscopic characteristics of HMs influence the transport of such contaminants into surrounding areas, which leads to environmental contamination (Caporale et al., 2016). It is known that the bioavailable fraction of HMs is fractions that can be quickly mobilized in the soil environment and taken up by plant roots. The residual fraction of the HMs is considered to be an unavailable biological form because they cannot be released into solution under a limited period in natural conditions (Borgese et al., 2013). Therefore, the bioavailability of HMs is related to their non-residual fractions and especially on exchangeable and carbonate fractions. Soil amendments can change the physicochemical properties of soil and impact the bioavailability of HMs. Despite the fact of bioavailability of HMs in contaminated soils, the simultaneous effects of organic, semi-organic, and inorganic amendments on HMs leaching and fractionations in a naturally contaminated site have not been investigated before.

We hypothesize that treated soils either with organic (biomass), semi-organic (biochar), or inorganic (industrial by-products) amendments, will reduce HMs leaching and the bioavailability by plants. Therefore, this study aimed to examine the attenuation capacity of varieties of soil amendments including rice husk (RRH), maple leaf (RML), rice husk biochar (RHB), maple leaf biochar (MLB), red mud (RM), or steel slag (SS) to mitigate HMs leaching, uptake, and translocation by lettuce in a post-mining soil. An emphasis was placed on easily leachable fractions (i.e., exchangeable and carbonate) of HMs. Besides, plant growth parameters were monitored during the experiment and under different experimental conditions.

2. Materials and methods

2.1. Soil and amendments preparation

The soil sample was collected from the surface soil (10–20 cm) of a farmland area in the vicinity of the Goepung abandoned mining site located in Okcheon County in South Korea (127044′14″ and 36019′49″) and sieved to soil fractions of <2 mm. The soil had a loamy sand texture (81% sand, 11% clay, and 8% silt), with a pH of 6.7 ± 0.05 and soil EC of 98 ± 3.5 μS m^{-1} (Table 1). Total organic carbon (TOM) and total nitrogen (TN) contents were 0.59 wt% and 0.04 wt%, respectively. Soil cation exchange capacity (CEC) was 7.6 ± 0.7 meq100 g^{-1}. Total concentration of As, Cd, Cu, Pb, and Zn in soil was 3.8 ± 0.10, 1.0 ± 0.02, 54.9 ± 2.10, 74.4 ± 1.80, and 291 ± 5.70 mg kg^{-1}, respectively.

Rice husk biomass was purchased from a commercial rice mill

Table 1
Physicochemical properties of the original soil and amendments.

Parameters	Original soil	RRH	RML	RHB	MLB	RM	SS
pH	6.7 ± 0.1	6.1 ± 0.0	5.3 ± 0.1	7.9 ± 0.1	8.9 ± 0.1	11.0 ± 0.1	12.0 ± 0.1
CEC (meq100g^{-1})	7.6 ± 0.7	7.6 ± 0.7	7.6 ± 0.7	7.6 ± 0.7	7.6 ± 0.7	7.6 ± 0.7	7.6 ± 0.7
ZP (mV) at pH = 7	ND	−23.0 ± 0.0	−25.0 ± 0.0	−35.0 ± 0.3	−28.0 ± 0.3	−15.0 ± 0.0	−21.0 ± 0.4
OM (wt.%)	0.6 ± 0.0	71.0 ± 1.5	71.0 ± 1.0	49.0 ± 0.5	21.0 ± 1.2	0.5 ± 0.0	0.9 ± 0.0
K (mgkg^{-1})	13.0 ± 0.5	9391 ± 26	3654 ± 12	2707 ± 15	2520 ± 23	48.0 ± 2.0	169 ± 5.0
TP (mgkg^{-1})	607 ± 8.0	25,968 ± 33	783 ± 10	48,714 ± 45	1379 ± 24	280 ± 7.0	4983 ± 18
TN (mgkg^{-1})	0.04 ± 0.0	0.5 ± 0.0	0.7 ± 0.0	3.3 ± 0.0	0.5 ± 0.0	0.01 ± 0.0	0.01 ± 0.0
SSA (m^2g^{-1})	ND	3.4 ± 0.1	5.3 ± 0.0	7.4 ± 0.7	12.0 ± 0.5	44.0 ± 2.5	18.0 ± 1.0
Conc. of metal(loid)s (mgkg^{-1})							
As	3.8 ± 0.1	0.6 ± 0.0	0.6 ± 0.0	0.4 ± 0.0	0.5 ± 0.0	2.6 ± 0.1	1.4 ± 0.0
Cd	1.0 ± 0.0	0.1 ± 0.0	1.0 ± 0.0	1.0 ± 0.0	0.4 ± 0.0	ND	ND
Cu	55.0 ± 2.1	11.0 ± 1.1	11.0 ± 0.1	18.0 ± 1.2	5.0 ± 0.5	15.0 ± 2.5	18.0 ± 1.8
Pb	74.4 ± 1.8	1.8 ± 0.3	0.8 ± 0.0	0.5 ± 0.0	0.5 ± 0.0	48.0 ± 3.2	18.0 ± 0.5
Zn	291 ± 5.7	15.0 ± 1.0	48.0 ± 4.3	16.0 ± 1.5	38.0 ± 3.0	131 ± 6.5	442 ± 10.0

RRH: raw rice husk, RHB: rice husk biochar, RML: maple leaf, MLB: maple leaf biochar, RM: red mud, SS, steel slag.
ND: not detected, ZP: zeta potential, OM: organic matter contents.

that processes white rice, one of the most popular rice in South Korea. The maple leaf was collected from the fallen leaf near the trees in the study area. Biomass feedstocks were thoroughly washed in the laboratory with tap water and finally with deionized water (DIW) and oven-dried (40 °C) for 4 d. Biochars were produced from those feedstocks in an anaerobic tube furnace (Wise-Therm(R) FT Programmable Tube Furnaces) under an $N_{2(g)}$ environment at 550 °C for 45 min. Red mud and steel slag which are by-products of alumina smelters company and steel industry, respectively, were purchased from commercial suppliers. Soil amendments were ground to have a fine particle size of <74 μm to modify their specific surface area (SSA) for the sorption of contaminants. Some of the physicochemical properties of the soil amendments are reported in Table 1. A Fourier-Transform Infrared (ATR-FTIR) spectrum to determine functional groups of the amendments and a scanning electron microscopy (SEM-EDS) to investigate the morphology of the amendments were obtained and the results are reported elsewhere (Derakhshan-Nejad and Jung, 2018b).

2.2. Experimental set-up

A pot experiment was conducted in a research greenhouse in the Sejong University, located in Seoul province, South Korea (Fig. S1). Experimental units consisted of plastic pots in a 25 × 23 cm in length and diameter, respectively, fitted with a bottom drainage container. Pots were filled with 1.0 kg of air-dried soil with a particle size of <2 mm and 300 g of washed sand to prevent soil compaction. To evaluate the effect of amending soil with amendments on the leachability and uptake of HMs by lettuce, soil amendments including i) RRH, ii) RML, iii) RHB, iv) MLB, v) RM, or vi) SS was added to the soil samples in each experimental pot at a rate of 1 and 2% w/w. Each mixture was individually prepared by thoroughly mixing. Before planting, the pots were incubated in the greenhouse for 65 d and left the mixtures to be equilibrated. A control pot was also prepared following the same procedure but without amending. Treatments were replicated three times. Totally, 39 pots were prepared for the experiment. The greenhouse temperature was 18–22 °C with 50% humidity. Three seedlings of the lettuce from unpolluted soils were transplanted in each experimental pots and watered 3 times a week (100 mLd^{-1}) with DIW (pH = 6.7). After 60 d planting, the plants were gently harvested and soil was collected.

2.3. Chemical analysis

Soil, leachate, and plant root and shoot samples were collected from each experimental pot and analyzed for physicochemical properties. Before analysis, roots were soaked in DIW to remove adhered soil. Roots and shoots were washed with DIW, oven-dried (40 °C) for 4 d, and powdered for chemical analysis. Soil and amendments pH and/or EC were determined in a solid to solution ratio of 1:5 using a multi-meter (Fisherbrand™ Accumet™ AB200, pH/EC Benchtop Meters, USA). Total concentrations of As, Cd, Cu, Pb, and Zn in the soil samples were determined using an aqua regia digestion method (Derakhshan-Nejad and Jung, 2017). Leachate samples were collected from the drainage container of each pot, filtered using Whatman paper no. 53 and acidified with 1 M HNO_3 to prevent any precipitation. Total concentrations of HMs in plant tissues were measured after hot digestion of samples (1 g) in 5 mL HNO_3 (70% w/w) for 1 h and a subsequent of adding 1 mL H_2O_2. The concentration of HMs in biochars were measured using a USA EPA method No. 1311. Concentrations of HMs in soil, amendments, leachates, and plants were measured by Atomic Adsorption Spectrometry (AAS; AA240, Varian, Australia). It is worthy to note that plants were harvested after 60 d and root samples were taken, as well. The concentration of HMs was measured in both plant leave and root.

The SSA of the amendments was measured by N_2 adsorption using a Micrometrics BET method by Tristar 3000, UK (Chen et al., 2012). For measuring soil and amendments CEC, 0.5 g of samples were washed four times with 4 mL of 1 M sodium acetate (CH3COONa) solution to exchange Na^+ ions with the matrix cations (Derakhshan-Nejad and Jung, 2018b). Subsequently, it was washed with ethanol (C2H5OH) to discard soluble exchangeable cations from the solution. Adsorbed Na^+ ions on exchangeable sites were then substituted with NH_4^+ ions three times using 3 mL of 1 M ammonium acetate (CH3COONH4). The concentration of Na^+ in the final solution was measured using AAS. Soil CEC was then calculated using Eq. (1).

$$CEC\ (meq/100g) = \frac{Na\ concentration\ (\mu g/ml)x\ dilution\ factor\ x\ 100(g)}{23\ (Na\ atomic\ weight)x\ 1000\ (Milli\ unit)} \tag{1}$$

Sequential extraction of HMs was measured based on Tessier et al. (1979), as an approach to evaluate metal distribution into easily/non-easily leachable fractions, before and after soil amending.

2.4. Data and statistical analysis

Translocation factors (*TF*) for HMs were calculated as follows (Hurtado et al., 2017):

$$TF = Cp \Big/ Cs\left(gg^{-1}dw\right) \tag{2}$$

where C_p is the concentration of an element in the plant tissue and C_s is the total concentration of the same element in the soil.

As a result of the soil treatments with amendments, the mobility of the soil metal(loid)s would be affected in the amended soils. To calculate metal(loid)s' immobilization ratio (%) at different experimental conditions, the following equation was applied (Wuana et al., 2013).

$$E(\%) = \left(\frac{M_{e-}M_0}{M_0}\right) \times 100 \tag{3}$$

where, M_o is the concentration of metals after harvesting in non-amended soils ($mgkg^{-1}$); M_e is the concentration of metals after harvesting in amended soils ($mgkg^{-1}$).

All the data in tables and figures correspond to the mean value of three replicates with standard deviation. The data were subjected to one-way analysis variance (ANOVA) using SPSS 16 on Windows 7. Two levels of significance were considered: $p < 0.1$ and $p < 0.05$.

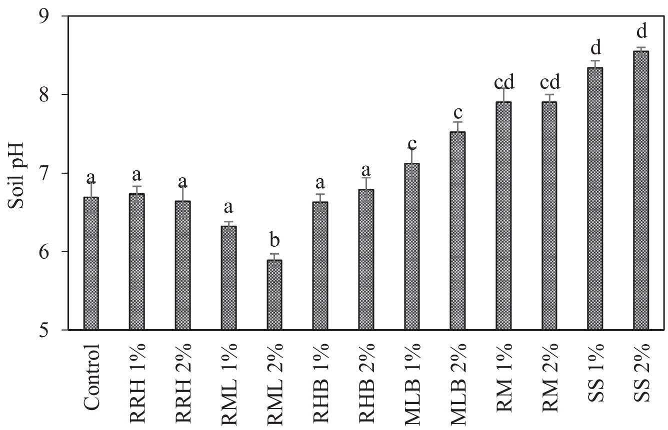

Fig. 1. Soil pH after 65 days incubation at experimental conditions.

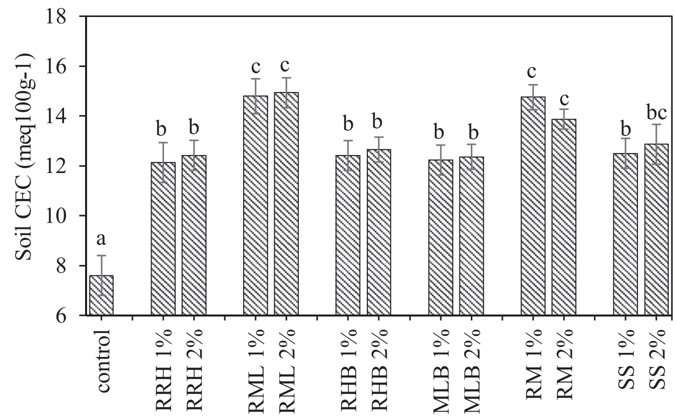

Fig. 3. Soil CEC after 65 days incubation at different experimental conditions.

3. Results

3.1. Changes in pH, EC, and CEC of the amended soil

The soil collected from agricultural soil around the mining site had a neutral pH. As it is shown in Fig. 1, soil pH significantly ($p < 0.05$) increased in MLB, RM, and SS amended soils from 6.7 ± 0.05 to 8.6 ± 0.05 after 65 d incubation. Increasing the application rates of MLB and industrial by-products led to an enormous (>1 unit) increase in soil pH. The maximum increase in soil pH was found for the soil amended with SS at a 2% w/w application rate (Fig. 1). On the contrary with MLB and industrial by-products, soil pH significantly ($p < 0.05$) decreased in RML amended soil (5.8 ± 0.08) especially at 2% w/w application rate. No significant change in soil pH was found for RRH and RHB amended soils.

Soil EC represents a measure of soluble nutrients including both cations and anions (Eigenberg et al., 2002). In the present study, soil EC was significantly ($p < 0.05$) increased in RRH (240 ± 4.2 μScm^{-1}), RML (251 ± 4.8 μScm^{-1}), and RM (136 ± 4.0 μScm^{-1}) amended soils at 1% w/w application rate after 65 d incubation (Fig. 2). However, no significant change in soil EC was found for biochars amended soils.

Soil CEC significantly ($p < 0.05$) increased in the amended soils with either organic, semi-organic, or inorganic amendments at a different rate (Fig. 3). The largest increase in soil CEC was found for RML (14.9 ± 0.5 meq100 g^{-1}) and RM (14.8 ± 0.3 meq100 g^{-1}) treatments. The application rate of the amendments did not significantly affect soil CEC values.

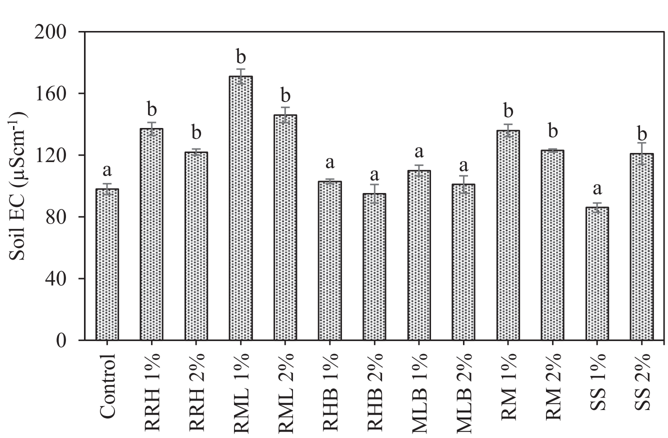

Fig. 2. Soil EC (μScm^{-1}) after 65 days incubation at experimental conditions.

3.2. Chemical speciation of metal(loid)s

The distribution of metal(loid)s in the amended/non-amended soils was examined using a sequential extraction method (Fig. 4 and S2). Since the bioavailability of HMs is related to easily leachable fractions, an emphasis was placed on the exchangeable and carbonate fractions of HMs (Fig. 4).

Based on the sequential extraction results, As, Cd, Cu, Pb, and Zn were associated more with the exchangeable fraction than with the carbonate fraction in the control soil, with average values of 6.7 ± 0.0, 45.5 ± 2.0, 12.4 ± 0.4, 12.4 ± 0.2, and 13.2 ± 0.5 mgkg^{-1}, respectively (Fig. 4). Adding biochars and industrial by-products showed promising results to reduce easily leachable fractions of HMs. Either organic, semi-organic, or inorganic amendments significantly ($p < 0.05$) reduced exchangeable (0.9 ± 0.26 vs. 6.7 ± 0.0 mgkg^{-1} in average) and carbonate (1.47 ± 0.39 vs. 4.1 ± 0.21 mgkg^{-1} in average) fractions of As.

Adding RML in the soil samples generated a significant increase in the amounts of an exchangeable fraction of Cd (73.6 ± 1.8 mgkg^{-1}). By contrast, the exchangeable fraction of Cd significantly decreased in the amending soil with RM (5.9 ± 0.9 mgkg^{-1}) and SS (6.0 ± 0.9 mgkg^{-1}). Adding RRH, RHB, MLB, RM, and SS increased the amounts of carbonate fractions of Cd from 14 ± 2 mgkg^{-1} to 32.7 ± 3.5, 24.6 ± 2.5, 26.3 ± 1.8, 34.2 ± 1.5, and 36.0 ± 2.1 mgkg^{-1}, respectively.

A great decrease in the amounts of easily leachable fractions of Cu was found after adding soil amendments. Amending soil with MLB significantly ($p < 0.05$) decreased exchangeable (0.15 ± 0.0 vs. 12.4 ± 0.4 mgkg-1) and carbonate fractions of Cu (2.6 ± 0.07 vs. 10.2 ± 0.34 mgkg^{-1}). By contrast, RHB amended soils generated a slight increase in the carbonate fraction of Cu (12.0 ± 0.6 mgkg^{-1}).

In comparison with the control soil, a meaningful ($p < 0.05$) decrease in the exchangeable fraction of Pb was found after amending soil with RM (1.7 ± 0.0 mgkg^{-1}) and SS (1.1 ± 0.2 mgkg^{-1}). In addition, carbonate fraction of Pb significantly decreased from 8.4 ± 1.1 mgkg^{-1} to 2.2 ± 0.1 and 2.6 ± 0.1 mgkg^{-1} for RM and SS treated soils after 65 d incubation.

The amounts of the exchangeable fractions of Zn significantly ($p < 0.05$) decrease to 0.01 ± 0.0, 0.6 ± 0.0, 0.7 ± 0.04, 0.86 ± 0.04 mgkg^{-1} in SS, RM, MLB, and RHB amended soils, respectively. In addition, a decrease was found in the amounts of carbonate fraction of Zn for RHB (2.07 ± 0.1 mgkg^{-1}), MLB (2.06 ± 0.2 mgkg^{-1}), RM (1.52 ± 0.06 mgkg^{-1}), and SS (2.47 ± 0.8 mgkg^{-1}) amended soils comparing with the control soil

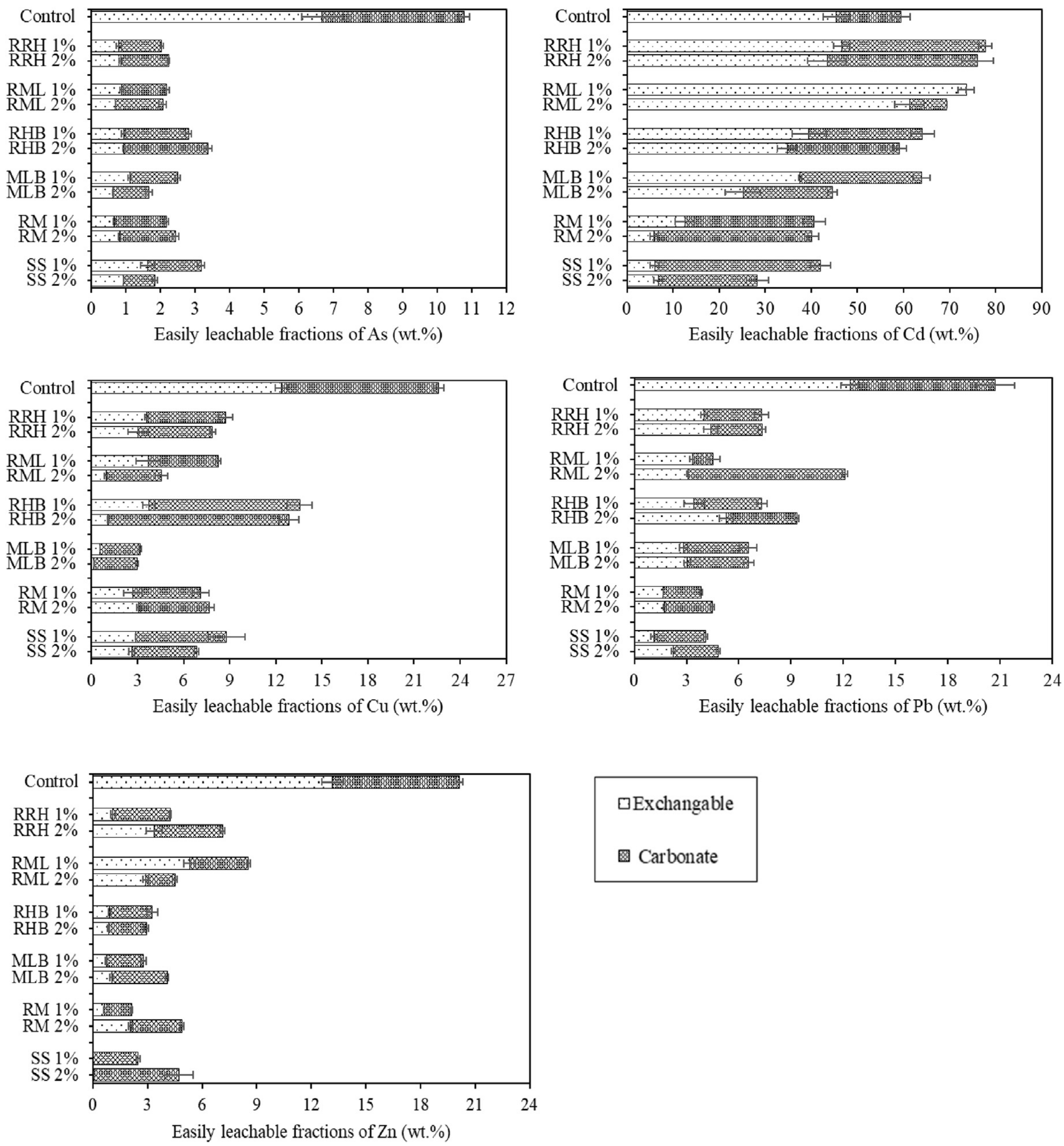

Fig. 4. Easily leachable fractions of heavy metal(loid)s after 65 days incubation at different experimental conditions.

(7.0 ± 0.2 mgkg^{-1}).

3.3. *Effect of soil amendments on HMs dynamics*

3.3.1. *Concentration of HMs in leachate*

The leaching of HMs was measured for different reaction times at different experimental conditions (Fig. 5). The concentration of HMs, except for As, in the leachates, increased with reaction time and application rate in RRH and RML amended soils. Amended soils with biochar and their feedstocks showed a significant ($p < 0.1$) decrease in As release with the maximum decrease for RML (0.0 ± 0.0 vs. 0.04 ± 0.0 mgkg^{-1}) with time and increasing application rate. Adding biochars and industrial by-products showed a gradual decrease in Cd leachability to approach 0.0 mgkg^{-1} after 60 d planting. Noteworthy, RRH and RML did not influence the leachability of Cd compared with that of the control samples. In comparison with control samples (0.011 ± 0.0), leachability of Cu decreased in biochars (0.002 ± 0.0 mgkg^{-1} in average) and industrial by-products amended soils (0.003 ± 0.0 mgkg^{-1} in average), while it increased in biomass amended soils (0.020 ± 0.0 mgkg^{-1} in average). The results indicated that the biochar and industrial by-products significantly decreased Pb and Zn leachability to approach 0.0 ± 0.0 mgkg^{-1} in SS amended soils These results are in agreement with the reduction of HMs availability indicated by the extractants in the sequential extraction method.

3.3.2. *Concentration of HMs in lettuce roots and shoots*

Fig. 6 shows concentrations of HMs in lettuce roots and shoots after 60 d planting. A small amount of As was found in the roots (0.6 ± 0.01 vs. 1.2 ± 0.04 mgkg^{-1}) and shoots (0.1 ± 0.01 vs. 0.4 ± 0.04 mgkg^{-1} in average) of lettuce after 60 d planting in RRH amended soil, while the other amendments did not affect As uptake

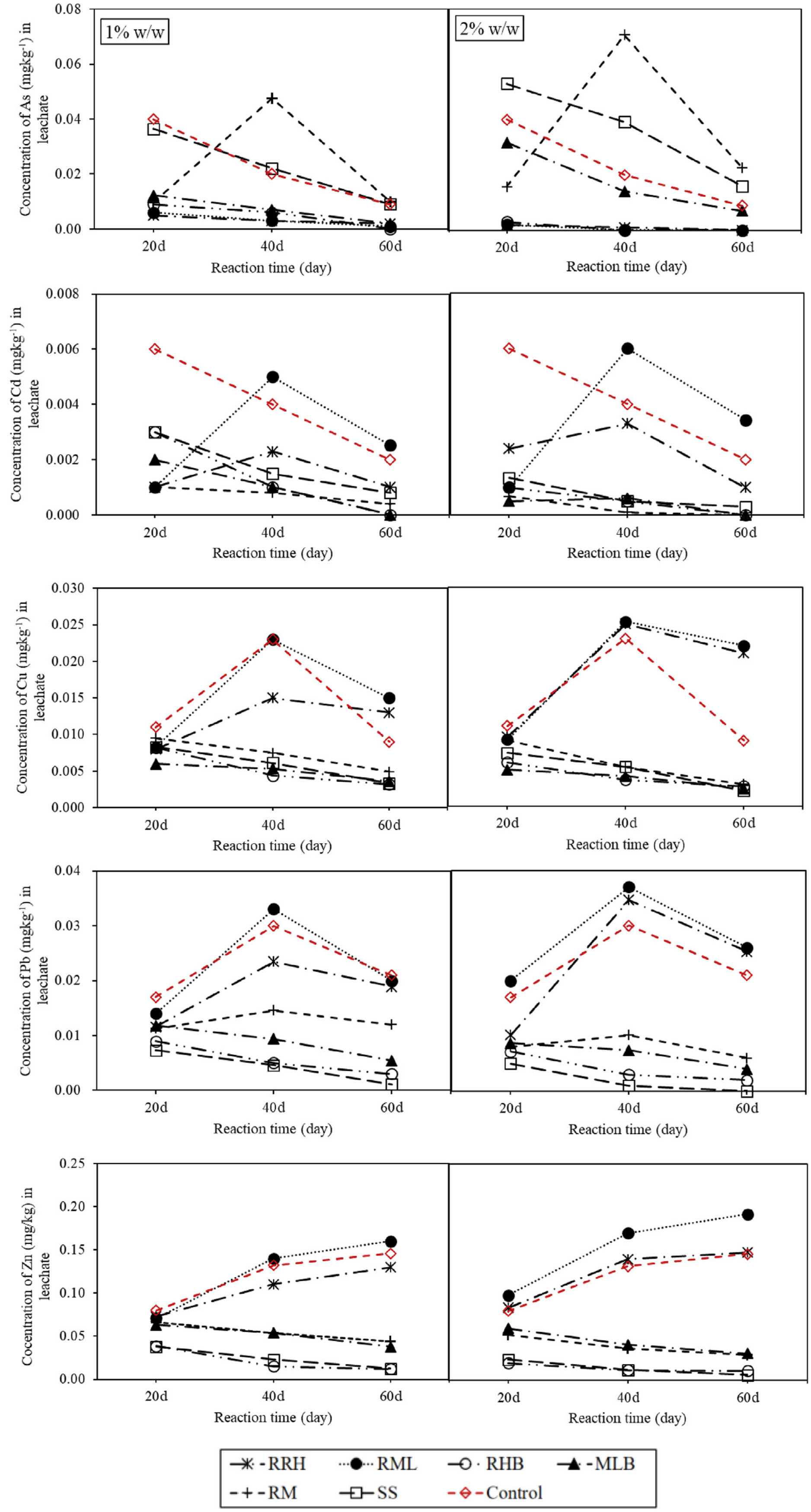

Fig. 5. Concentration of heavy metal(loid)s in leachate during the experiment.

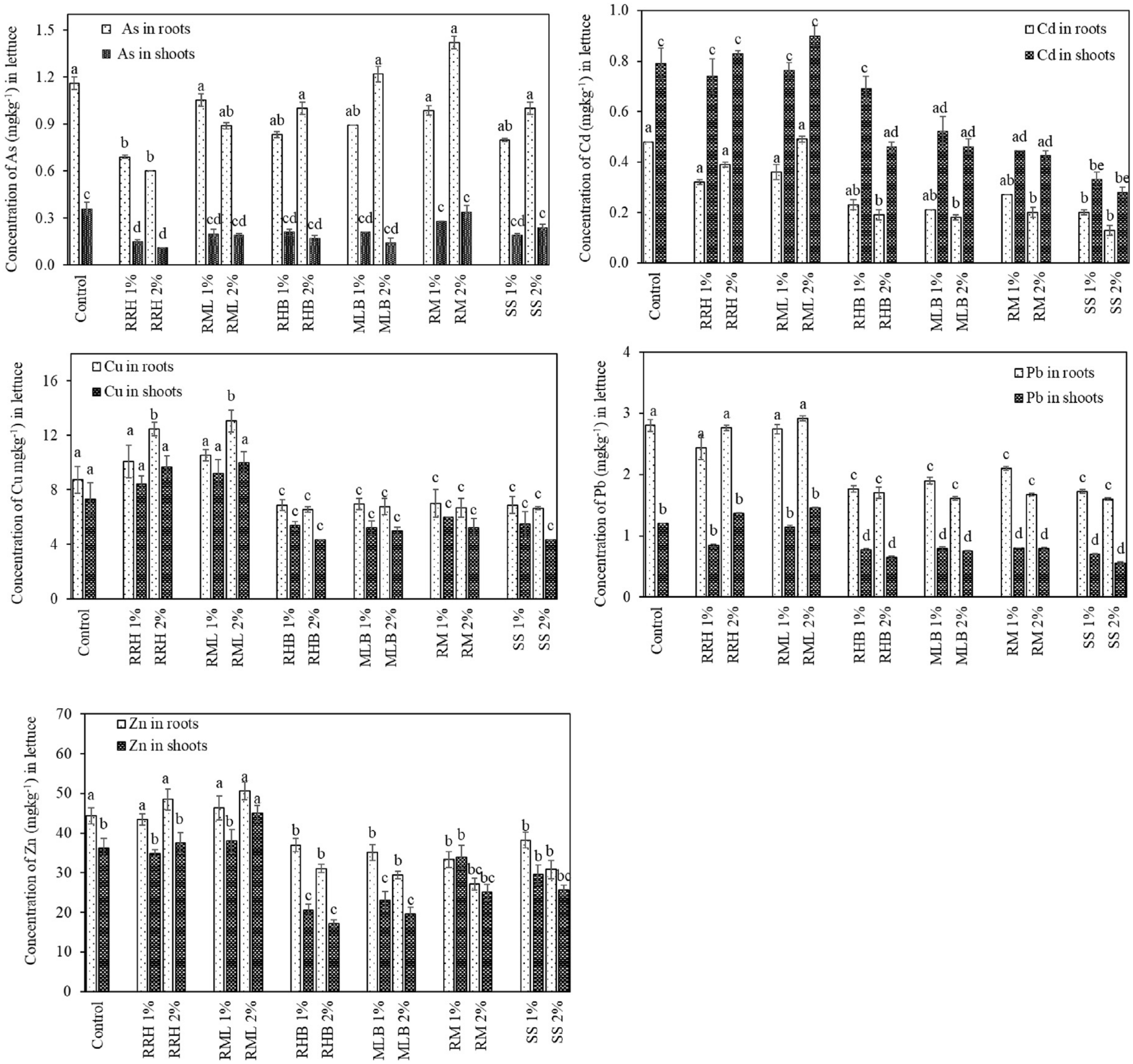

Fig. 6. Concentration of heavy metal(loid)s in lettuce roots and shoots at experimental conditions after 60 days of planting.

Table 2
Translocation factor from soil to lettuce after 60 days planting (±STD).

Treatments	Elements				
	As	Cd	Cu	Pb	Zn
RRH 1%	0.05 ± 0.00^{a}	1.86 ± 0.04^{ab}	0.35 ± 0.01^{a}	0.03 ± 0.00^{a}	0.18 ± 0.05^{a}
RRH 2%	0.03 ± 0.00^{b}	2.30 ± 0.06^{b}	0.43 ± 0.01^{b}	0.04 ± 0.00^{a}	0.21 ± 0.03^{a}
RML 1%	0.06 ± 0.01^{a}	1.96 ± 0.04^{a}	0.40 ± 0.02^{b}	0.03 ± 0.00^{a}	0.24 ± 0.03^{a}
RML 2%	0.06 ± 0.00^{a}	3.00 ± 0.10^{b}	0.47 ± 0.01^{b}	0.04 ± 0.00^{a}	0.31 ± 0.02^{b}
RHB 1%	0.07 ± 0.01^{ac}	0.92 ± 0.03^{c}	0.16 ± 0.00^{c}	0.01 ± 0.00^{b}	0.10 ± 0.00^{c}
RHB 2%	0.05 ± 0.01^{a}	0.51 ± 0.00^{cd}	0.11 ± 0.00^{c}	0.01 ± 0.00^{b}	0.10 ± 0.01^{c}
MLB 1%	0.07 ± 0.00^{ac}	0.67 ± 0.05^{c}	0.16 ± 0.03^{c}	0.01 ± 0.00^{b}	0.10 ± 0.00^{c}
MLB 2%	0.05 ± 0.00^{a}	0.52 ± 0.02^{cd}	0.12 ± 0.01^{c}	0.01 ± 0.00^{b}	0.10 ± 0.0^{c}
RM 1%	0.08 ± 0.01^{ac}	0.54 ± 0.02^{cd}	0.19 ± 0.00^{c}	0.01 ± 0.00^{b}	0.15 ± 0.03^{c}
RM 2%	0.10 ± 0.01^{ac}	0.49 ± 0.02^{d}	0.13 ± 0.00^{c}	0.01 ± 0.00^{b}	0.10 ± 0.02^{c}
SS 1%	0.06 ± 0.01^{a}	0.49 ± 0.0^{d}	0.16 ± 0.02^{c}	0.01 ± 0.00^{b}	0.11 ± 0.01^{c}
SS 2%	0.08 ± 0.00^{ac}	0.31 ± 0.02^{d}	0.11 ± 0.01^{c}	0.01 ± 0.00^{b}	0.10 ± 0.00^{c}
Control	0.12 ± 0.01^{c}	2.82 ± 0.08^{b}	0.31 ± 0.05^{a}	0.03 ± 0.00^{a}	0.21 ± 0.03^{a}

Numbers with the same letter in each column are not significantly different.
RRH: raw rice husk, RHB: rice husk biochar, RML: maple leaf, MLB: maple leaf biochar, RM: red mud, SS, steel slag.

by lettuce. The average *TF* to lettuce shoots for As in the control samples was 0.12 ± 0.01 gg^{-1} dw and it decreased to 0.03 ± 0.00 gg^{-1} dw in RRH amended soils but ranged from 0.05 ± 0.00 to 0.10 ± 0.01 gg^{-1} dw among different soil amendments (Table 2).

Among soil HMs, a higher concentration for Cd was found in lettuce shoots than roots. Amending soil with biochars and industrial by-products caused a reduction in Cd uptake by lettuce roots (0.20 ± 0.04 vs. 0.50 ± 0.00 $mgkg^{-1}$ in average) and shoots (0.40 ± 0.10 vs. 0.80 ± 0.06 $mgkg^{-1}$ in average). The average *TF* for Cd in the control samples was 2.82 ± 0.08 gg^{-1} but ranged from 0.31 ± 0.02 in SS to 3.00 ± 0.10 gg^{-1} in RML amended soils.

Amending soil with biochars and industrial by-products resulted in a reduction in Cu uptake by lettuce roots (6.8 ± 0.10 vs. 8.7 ± 1.00 to $mgkg^{-1}$ on average) and shoots (5.10 ± 0.53 vs. 7.30 ± 1.20 $mgkg^{-1}$ on average), while it induced Cu uptake and accumulation in lettuce roots in RRH (12.5 ± 0.70 $mgkg^{-1}$) and RML amended soils (13.0 ± 0.60 $mgkg^{-1}$) at 2% w/w application rate. The average *TF* for Cu in the control samples was 0.31 ± 0.05 gg^{-1} and ranged from 0.11 ± 0.00 for SS to 0.47 ± 0.01 gg^{-1} dw for RML at a 2% w/w application rate.

A great decrease was found for Pb uptake in lettuce roots (1.70 ± 0.20 vs. 2.80 ± 0.10 $mgkg^{-1}$ on average) and shoots (0.60 ± 0.05 vs. 1.20 ± 0.00 $mgkg^{-1}$ on average) in biochars and industrial by-products amended soils, but not for that of the organic amended soils. The average *TF* for Pb in the control samples was 0.03 ± 0.00 gg^{-1} and slightly decreased to 0.01 ± 0.00 for alkaline amended soils.

A smaller amount of Zn was found in lettuce roots (31.0 ± 3.50 vs. 44.3 ± 2.00 $mgkg^{-1}$ on average) for biochars and industrial by-products amended soils. Amending soil with RHB and MLB resulted in a reduction in Zn uptake by lettuce shoots (20.0 ± 2.10 vs. 36.0 ± 2.40 $mgkg^{-1}$ on average). The average *TF* for Zn in the control samples was 0.21 ± 0.03 gg^{-1} and ranged from 0.10 ± 0.00 for alkaline amendments to 0.31 ± 0.2 gg^{-1} for RML at a 2% (w/w) application rate.

3.4. Plant growth parameters under different experimental conditions

Results reveal that the response of lettuce to amendment application varied between amendments type and application rates (Table 3). Amending soil with organic amendments and biochars significantly ($p < 0.1$) induced plant growth parameters. After 60 d planting, a great increase in the number of lettuce leaves was especially found for RRH 2% (46 ± 3.6) and RML 1% (43 ± 4.6), comparing with the control samples (28 ± 2.2). Noteworthy, RHB and SS also induced the number of lettuce leaves with less significant numbers ranged from 42 ± 3.3 to 32 ± 0.0, respectively. Comparing with the control samples (12 ± 1.1 cm), lettuce length significantly increased in RML 2% (16 ± 1.7 cm), RHB 1% (16 ± 1.3 cm), and MLB 1% amended soils (16 ± 1.4 cm). Amending soil with biochars meaningfully increased plant weight from 2.6 ± 0.2 g in the control samples to 4.4 ± 0.1 and 4.7 ± 0.3 g in RHB and MLB, respectively. After 60 d planting, lettuce roots length in the control samples was 8.0 ± 0.6 and it significantly increased in RRH 1% (10 ± 0.6 cm), RML 1% (10 ± 0.6 cm), RHB 2% (14 ± 0.7 cm), and MLB 2% amended soils (14 ± 0.3 cm).

4. Discussion

4.1. Physicochemical properties of soil

Soil CEC meaningfully increased after adding biochars, RM, and SS. It is attributed to the release of a great number of cations, e.g., Ca^{+2} and Mg^{+2} on the corresponding amendments surface which can be exchanged with metal ions and subsequently increase soil CECs (Li et al., 2015, 2016). Previous studies have shown that a decrease in the solubility and leachability of HMs in soils following increasing application rates of biochar or inorganic amendments are probably related to the high number of cation exchange sites on their surfaces (Harvey et al., 2011; Li et al., 2016). In addition, oxygen-containing functional groups in amendments, carboxyl groups (-COOH) in particular, adsorb metal ions through ion exchange processes (Ho et al., 2017).

In our study, soil EC was increased in the amended soils which were mainly attributed to an increase in the soil ionic concentration. Soil EC is an index used to delineate site-specific management zones since it is highly correlated to crop yield and can be considered as a soil fertility index (Li et al., 2008). Soil EC is a function of the ionic concentration in a media and is related to the electrical surface charges density at the surface of the constituents. Since total salinity and ion composition in the soil are the two most important 12 factors affecting soil EC (Liu et al., 2006), EC can be a good measure of not only the total salinity but also of the ion composition in the soil water. A combination of the EC and CEC measurements in our study can constrain uncertainties associated with individual measurements and increase the reliability of the results for land management.

According to Tandon et al. (2008), materials showing a ZP of 22 mV (positive or negative) have highly charged surfaces; this can be considered the conventional value that separates low-charged surfaces from high-charged surfaces. In our study, all the soil amendments showed values for zeta potential (ZP) higher than 22 mV (positive or negative) in their original pH range (Table 1). The ZP values for all amendments were predominantly negative in the studied pH range, which indicated that particles of the amendment carried negative charges on their surfaces, which was suitable to absorb and stabilize soil HMs (Tong et al., 2011).

Table 3
Influence of amendments on lettuce growth parameters after 60 days planting (±STD).

Soil treatments (g/kg)		Leaf number	Leaf Length (cm)	Plant weight (g)	Root Size (cm)
RRH	1%	41 ± 4.2 ^{bc}	11 ± 1.2^{a}	3.1 ± 0.3 ^{ab}	10 ± 0.6^{b}
	2%	**46** ± 3.6^{c}	14 ± 1.6 ^{ab}	3.5 ± 0.2^{b}	9 ± 0.5^{a}
RHB	1%	35 ± 2.8^{b}	**16** ± 1.3^{b}	**4.4** ± 0.1^{c}	13 ± 0.7 ^{bc}
	2%	42 ± 3.3 ^{bc}	13 ± 2.0 ^{ab}	2.9 ± 0.3^{a}	**14** ± 0.7^{c}
RML	1%	**43** ± 4.6 ^{bc}	14 ± 1.3 ^{ab}	3.3 ± 0.5^{b}	10 ± 0.6 ^{ab}
	2%	36 ± 3.7^{b}	**16** ± 1.7^{b}	3.7 ± 0.2^{b}	8 ± 0.4^{a}
MLB	1%	34 ± 3.2^{b}	**16** ± 1.4^{b}	**4.7** ± 0.3^{c}	13 ± 0.7 ^{bc}
	2%	37 ± 3.6^{b}	13 ± 1.4 ^{ab}	3.6 ± 0.5^{b}	**14** ± 0.3^{c}
RM	1%	39 ± 2.1^{b}	11 ± 1.1^{a}	2.2 ± 0.0^{a}	7.4 ± 0.5^{a}
	2%	34 ± 1.8^{b}	13 ± 1.5 ^{ab}	2.5 ± 0.3^{a}	9.1 ± 0.8^{a}
SS	1%	32 ± 0.0^{b}	12 ± 2.2^{a}	2.7 ± 0.4^{a}	10 ± 0.4^{b}
	2%	36 ± 2.3^{b}	12 ± 1.0^{a}	2.4 ± 0.2^{a}	9.5 ± 0.5^{a}
Control	0	28 ± 2.2^{a}	12 ± 1.1^{a}	2.6 ± 0.2^{a}	8.0 ± 0.6^{a}

* Highest level of growth parameters was bolded.
RRH: raw rice husk, RHB: rice husk biochar, RML: maple leaf, MLB: maple leaf biochar, RM: red mud, SS, steel slag.

Literature showed that the high electronegativity of biochar can simplify the electrostatic attraction of positively charged ions (Ahmad et al., 2016; Derakhshan-Nejad and Jung, 2018a). Its intensity depends on the surface charge generated by the surface negatively charged surface groups, which became increasingly negative at higher pH (Faria et al., 2004). The electrostatic adsorption also increases with initial concentrations of HMs (Dai et al., 2015, 2017).

On the other hand, previous studies showed that biomass and its derived biochar had a fraction soluble of organic carbon that can be utilized by microorganisms and mineral carbonate, which can enhance plant growth and yield (Ye et al., 2019; Videgain-Marco et al., 2020). Jiang et al. (2012) also observed that dissolved organic carbon (DOC) in a soil amended with plant-derived biochars could be rapidly degraded by soil microbes and induce soil fertility. Since we did not investigate DOC after adding amendments in our study, it could be only speculated that the plant growth has been stimulated after adding biomass and biochar due to the subsequent effect on soil DOC. Besides to an induce in the plant growth and yield, soil phytoavailable metal pools following the addition of amendments decreased in the amended soils, which can cause a reduction in phytotoxicity and subsequently improving the development of plants (Oni et al., 2019).

4.2. Soil HMs leaching behaviors at different experimental conditions

Application of soil amendments reduced the concentration of HMs in the leachates. In the amended soil, this may happen if the amendment provides binding sites for the HMs or by altering the soil chemistry (Hamid et al., 2018). To compare soil HMs' leaching behaviors in the amended soils with the non-amended samples, each data set of metal(loid)s concentration was plotted in x (non-amended) and y (amended) plane, and the distribution of each metal(loid)'s concentrations was observed with a 1:1 regression line (Fig. 7). If the data points were consistently distributed under

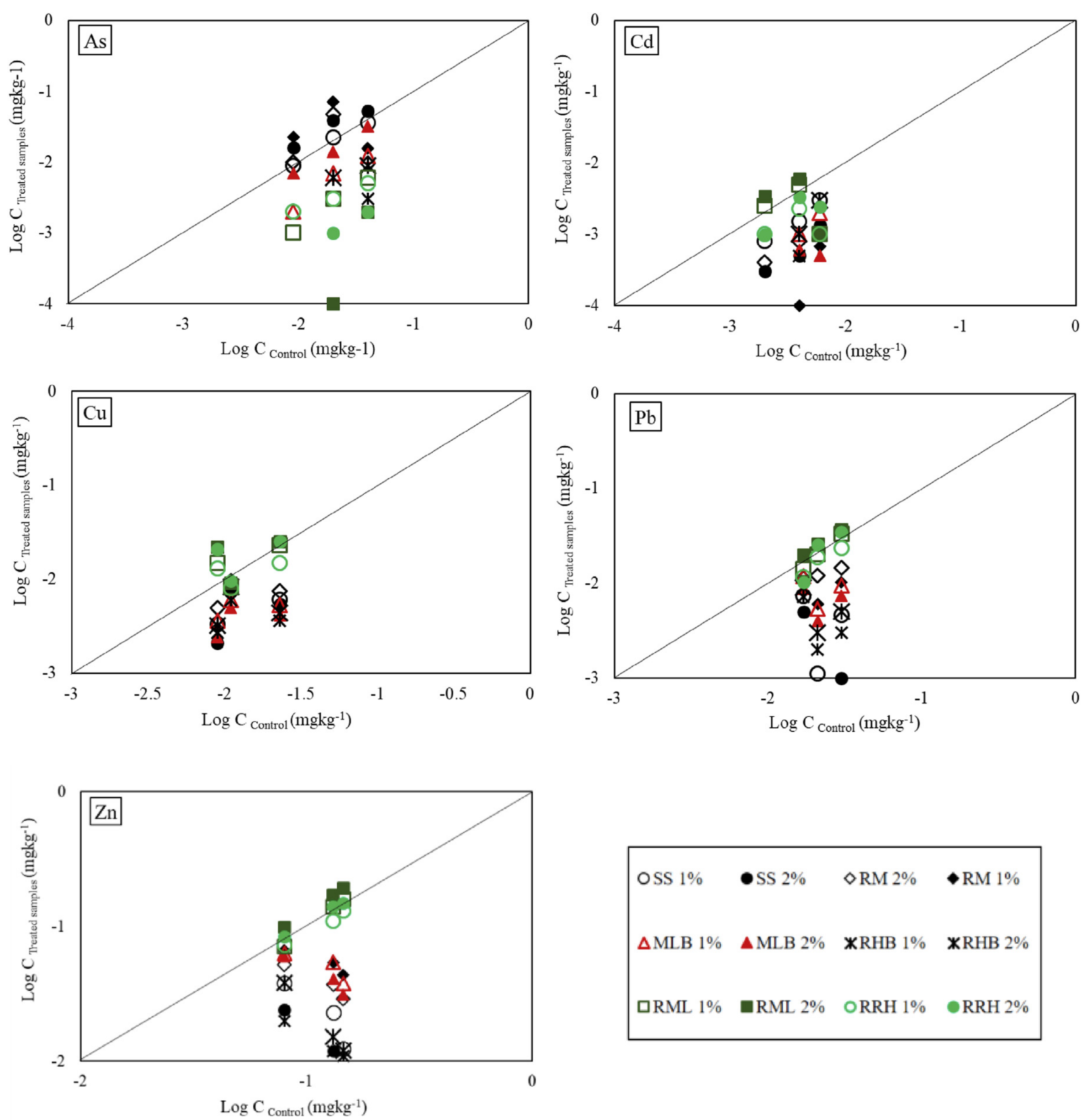

Fig. 7. Impact of the soil amendments on the metal(loid)s leaching behavior (a comparison between leachates of control and treated samples).

the 1:1 line, then the metal(loid)s were stabilized and immobilized in soil by which the leachability of HMs from soil to the leachate decrease. In our study, RM and SS induced the release of As from soil to leachate, while biochars and their feedstocks reduced As leachability (Fig. 7). Amended soils with biochars, RM, and SS reduced the leachability of Cd, Cu, Pb, and Zn and stabilized them in the treated soils mainly due to their alkaline pH.

The results presented above show that pH increased by the addition of semi-organic (biochars) and inorganic (industrial by-products) amendments led to an enhanced immobilization of Cd, Cu, Pb, and Zn, while organic (biomass) amendments decreased soil pH and induced immobilization of As in soil. Soil pH is a key factor controlling the speciation and mobility of metals (Derakhshan-Nejad et al., 2017). Biochar, RM, and SS are alkaline and could thus increase soil pH with increasing application rates, particularly in acid soils (Dai et al., 2017; Yu et al., 2019). This could in turn increase the hydrolysis of HMs, enhance their adsorption by soil, and accelerate the transformation of the oxidizable and residual fractions of HMs. The increased pH could also increase HMs complexation, decreasing the desorption of Cd, Cu, Pb, and Zn from soils (Jiang et al., 2012; Derakhshan-Nejad et al., 2017). The increases in soil pH following biochar, RM, and SS amendments therefore mitigated the risks of HMs. The increase of pH in the biochars and industrial by-products amended soils was attributed to the effect of soluble carbonates and the base cations (e.g. K, Ca, Na, Mg) as well as surface functional groups in the soil amendments (Li et al., 2016).

4.3. Stabilization mechanisms for soil HMs

Possible mechanisms for the HMs retention in soil by alkaline amendments could be the formation of metal (hydr)oxide, carbonate, or phosphate precipitates and/or the activation of surfaces caused by the pH rise, specific metal-ligand complexation involving surface functional groups (particularly oxygen, phosphorus, sulfur, and nitrogen functional groups) that may or may not involve cation exchange. The functional groups (e.g., eOH, eCOOH, eCO-, CH, C=C, and Si—O) in RHB, MLB, RM, and SS (see the paper published by Derakhshan-Nejad and Jung, 2018b) provide binding sites for HMs to form complexes and subsequently increase the specific adsorption of HMs (Qian and Chen, 2013). It is known that the biochars with high CaO contents have higher adsorption capacity mainly due to the formation of Ca and Si complexes (e.g., $2CaO*SiO_2$) in neutral media (Derakhshan-Nejad et al., 2017). Among the soil amendments in the present study RML, MLB, and SS showed a great content of CaO contents (Derakhshan-Nejad and Jung, 2018b).

The ability of amendments to complex HMs increases with increasing Fe (II), Mn (II), and carbonate concentrations, resulting in the formation of insoluble and stable metal complexes (Ahmad et al., 2016). Also, inorganic ions (e.g., Si, S, and Cl) contained in biochar can complex with HMs, e.g., Cd, decreasing their mobility in soil. Besides, the mineral elements contained in soil amendments may precipitate with metals, forming insoluble precipitates (Cao and Harris, 2010). Soil metals can precipitate as pure solids (e.g., MCO_3, $M(OH)_2$, MS_2) or co-precipitate producing mixed solids (e.g. $(Fex, Cr1\text{-}x)(OH)_3$). By the way, complexation is likely important for metalloid ions such as As which have a high affinity for specific ligands (e.g., phosphate) on the surface of either biomass or its derived chars and can result in precipitation, as it was observed before for As immobilization by rice husk biomass or rice biochar (Derakhshan-Nejad et al., 2016).

4.4. Soil HMs immobilization efficiency

The immobilization of As increased to 20% with increasing application rates of RRH, RML, and RHB (Fig. 6). By contrast, increasing application rates of MLB, RM, and SS decreased immobilization efficiency for As in the amended soils. An increase in application rates of biochars, RM, and SS induced immobilization 15 efficiency for Cd, Cu, Pb, and Zn with the maximum values of 62, 72, 89, and 58%, respectively. With an increase in application rates of RRH and RML, mobilization of Cu, Pb, and Zn slightly increased, which induced the bioavailability of HMs for plants. In our study, the considerable immobilization capacity of biomass for As highlights the roles of non-carbonized biomass fractions in As immobilization. So, the effectiveness of soil amendments strongly depended upon the type of metal contaminant.

Indeed, choosing appropriate application rates for soil amendments in agricultural soils is a critical factor for controlling soil pH and plant growth. Regarding environmental safety and economic purposes, a small application rate (i.e., 1 and 2% w/w) for soil amendments was chosen in the present study comparing with the literature (NamKoong and Jeong, 2012; Wuana et al., 2013; Zheng et al., 2013; Ahn et al., 2015; Kim et al., 2015; Derakhshan-Nejad and Jung, 2018b). In our study, a physical change in particle size fractions of soil amendments induced their capability for HMs sorption. Although we applied a small rate for amendments, our results were a great match with the previous studies that applied a great number of soil amendments (>5 wt%) for HMs immobilization.

5. Conclusion

This study examined the effect of different varieties of soil amendments on the HMs leaching and bioavailability and its subsequent influence on the plant growth in contaminated soil around a mining site. The conclusions of the present study are as follows.

- Biochars and inorganic amendments at a 2% w/w application rate induced Cd, Cu, Pb, and Zn immobilization by 62, 72,89, and 66 wt%, respectively, while As was mostly immobilized in organic amended soils by 19 wt%.
- Biochars, RM, and SS amendments decreased the bioavailability of HMs as supported by mechanisms that involve direct (e.g., ion exchange, electrostatic adsorption, precipitation/co-precipitation, and complexation) and indirect interactions (through modifying soil physicochemical properties such as pH, CEC, etc.) between soil amendments and HMs.
- The application of biochars with fine particles to agricultural soils showed the potential for a great improvement in soil physical, chemical, and biological conditions, which caused an increase in the final plant height, plant weight, root size, and the number of leaves in lettuce.
- The addition of biomass in soil tremendously induced soil fertility and plant growth.

Our study supports the need for further research into the long-term impacts of either biochars or industrial alkaline by-products in soils to mitigate HMs leaching and bioavailability.

Declaration of competing interest

I am Zahra Derakhshan Nejad the corresponding author of the paper entitled “Effects of environmentally friendly soil amendments on the mitigation of heavy metal(loid)s leaching and bioavailability in a post-mining area” declare that there is no conflict of interest for this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.129538.

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