

Research Article

Potential for Lead Release from Lead-Immobilized Animal Manure Compost in Rhizosphere Soil of Shooting Range

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This study aimed to clarify the magnitude of lead release from lead-sorbed animal manure compost (AMC) in rhizosphere soil compared with nonplanted soil of shooting range. The presence of buckwheat caused reduction in rhizosphere soil pH and enhancement in the level of water-soluble organic carbon compared with those of nonplanted soil. In addition, the presence of buckwheat altered the lead phases and increased the relative amount of the soluble exchangeable fraction, resulting in increase in the CaCl₂-soluble lead level. In contrast, the presence of Guinea grass did not change the lead bioavailability or phases compared with nonplanted soil. Lead release tests in solution showed that between solution pH 5 and solution pH 7 the amount of lead released from the compost was higher in the rhizosphere soil of buckwheat than in nonplanted soil, whereas there was no significant difference between the rhizosphere soil of Guinea grass and nonplanted soil. These results suggest that the increase in the quantity of exchangeable lead resulting from the rhizosphere effect induces lead immobilized by the AMC to be remobilized. Therefore, AMC should be applied to soils that contain plants that are unable to alter the lead phases in the shooting range soil. Efforts should be particularly made to ensure that lead cannot be transformed to the exchangeable phase.

1. Introduction

In the soil of shooting ranges, lead derived from spent bullets typically accumulates at a very high concentration, causing heavy lead contamination in the soil. Shooting activity has continued in Tajimi shooting range in Gifu, Japan; however, its activity has been prohibited after the detection of heavy lead contamination in the shooting range. A typical method of remediation of toxic-metal-contaminated soil is excavation and transport to landfill sites in Japan. However, shooting ranges have an extensive area and a very low asset value due to their location away from residential areas. Thus, this method could not be applied due to its relatively high cost, which resulted in prohibiting entry into the shooting range.

Chemical immobilization techniques represent a simple and eco-friendly approach for the prevention of toxic metal leaching from contaminated soils. Since the toxic metals

are not removed from the soil following immobilization, remaining instead in the soil, better understanding of the immobilization mechanisms, that is, the formation of insoluble phases by the material and the subsequent dissolution of the toxic metals from the material following changes in soil parameters such as soil pH and oxic-redox conditions, is important to enhance the reliability of immobilization techniques [1].

Animal manure is the most abundant organic waste material and is mainly generated from cattle, swine, and poultry farms in Japan. The quantity of animal manure generated annually is estimated at 8.0×10^7 tons as fresh weight, which corresponded to about 25% of organic waste material in Japan [2]. Thus, it is necessary to recycle animal manure to reduce the waste material. Animal manure compost (AMC) has been studied to evaluate its potential use as an immobilization material [3–7]. AMC not only has the ability to immobilize

TABLE 1: Selected physicochemical properties of the soil used in this study (dried weight basis).

Sand (%)	Silt (%)	Clay (%)	pH	EC (mS m ⁻¹)	TC (mg g ⁻¹)	TN (mg g ⁻¹)	WSOC* ¹ (mg kg ⁻¹)	Total Pb (mg kg ⁻¹)	Amorphous Fe (mg g ⁻¹)
46	27	27	6.9	3.4	16.1	1.3	138	21	3

*¹Water-soluble organic carbon.

toxic metals in soils [3–7] but also has advantages that inorganic immobilization materials do not have; that is, AMC contains organic matter and nutrients that can stimulate plant growth and microbial activity in soils that have been affected by metal toxicity [8–11]. Although these advantages may encourage the application of AMC onto contaminated soils, less is known about the mechanisms of immobilization by AMC [12, 13] compared with other inorganic and organic waste materials [14], particularly the applicability of AMC to the shooting range soil and the remobilization of lead that was once immobilized by AMC.

Katoh et al. [13, 15, 16] conducted several studies to elucidate the mechanisms of lead immobilization by AMC using the inorganic and organic components of specifically fractionated AMC to understand the suitable chemical properties of AMC to immobilize lead present in the shooting range soil. The studies revealed that the inorganic components in AMC can immobilize lead more effectively than the organic components [13]. A high phosphorus content in the inorganic components of swine manure compost effectively immobilized lead because of the precipitation of lead phosphate minerals that have low solubility products. In addition, maturation of cattle manure makes the organic components more suitable for lead immobilization because of the resulting decrease in water-soluble organic matter, which can enhance lead mobility. On the basis of these results, Katoh et al. [13, 15] suggested that compost that contains an inorganic content with a high phosphorus level, such as swine manure compost, and an organic component that has undergone maturation, such as cattle manure compost, was the most suitable to immobilize lead in soils. In addition, they pointed out that inorganic/organic components ratio of 25:75 was suitable to both immobilize lead and restore microbial activity in the shooting range soil [16]. Furthermore, it was demonstrated that such AMC can reduce lead bioavailability in the soil, resulting in a reduction in lead uptake by plants [15]. However, these results do not enhance the reliability of AMC as an immobilization material because lead, once immobilized, might be remobilized by changes in the soil environment [17].

The interface between the soil and the plant is known as the rhizosphere; in this region, root activity greatly influences the soil environment. The physical, chemical, and biological properties of the rhizosphere soil are different from those of the soil that does not contain plants. The plant roots penetrate the soil and exude organic matter such as organic acids, sugars, amino acids, and enzymes, which change the soil pH, redox potential, microbial activities, biomass, organic matter content, and the chemical speciation of elements [18]. Thus, lead immobilized by the inorganic and organic components in AMC has the potential to be remobilized in the rhizosphere

soil. For example, the decomposition of organic matter by microorganisms leads to the enhanced release of lead sorbed onto the organic matter [19]. Larger quantities of lead are dissolved from pyromorphite in the presence of an organic acid than in the presence of water, even though pyromorphite is one of the most stable lead minerals [20]. Furthermore, pH changes influence the sorption/desorption behavior of lead onto inorganic and organic materials in soil [21, 22]. Therefore, if lead immobilized onto AMC is exposed to rhizosphere effects, lead may be remobilized; however, to the best of our knowledge, the degree to which this occurs has not been investigated. There is a need to investigate the rhizosphere effect on lead immobilization to enhance the reliability of immobilization by AMC because the lead once immobilized by AMC is exposed to the rhizosphere effect of native plant in the shooting range soil.

We have investigated the bioavailability, phases, and release characteristics of AMC-sorbed lead in rhizosphere soil in which plants with either high or low tolerance to lead toxicity were grown. We aimed to clarify the magnitude of lead release from lead-immobilized AMC in rhizosphere soil compared with that in bulk soil. On the basis of the results obtained, we discuss lead immobilization techniques using AMC in the shooting range soil.

2. Materials and Methods

2.1. Soil Preparation. Brown forest soil with a light clay texture was collected from 5–15 cm depths from 35°22'13''N, 137°8'42''E in Tajimi, Gifu, Japan, and used as the basic soil for plant cultivation. The sampling site was located near a shooting range but was not contaminated by lead. Before use, the soil pH was adjusted to 7 using calcium carbonate. This was done to adjust the soil pH to match that of the compost used, because pH significantly enhances or reduces lead mobility and bioavailability [23]. The soil was air-dried, passed through a 2 mm sieve, and kept at room temperature prior to the cultivation tests. Table 1 shows selected chemical properties of the soil. The total lead content of the soil was equal to the background level of 21 mg kg⁻¹ and the final soil pH was 6.9.

2.2. Fractionation of Inorganic and Organic Components and Preparation of Lead-Sorbed Simulated Compost. In this study, the compost was prepared by mixing the inorganic fraction of swine manure compost and the acid-insoluble organic fraction of cattle manure compost. We selected these compost fractions since each fraction can immobilize lead more effectively and strongly than other composts [13]. Commercial swine and cattle manure compost (Fujimi Kogyo Co., Japan) were used to obtain the inorganic and acid-insoluble organic

TABLE 2: Selected chemical properties of the lead-sorbed inorganic and organic compost fractions used in this study (dried weight basis).

Fraction	WSOC* ¹ (mg kg ⁻¹)	Pb (mg g ⁻¹)	Total			
			C (mg g ⁻¹)	N (mg g ⁻¹)	Ca (mg g ⁻¹)	P (mg g ⁻¹)
Inorganic fraction	ND* ²	171	ND	ND	114	92.9
Organic fraction	1330	27.2	447	18.2	0.2	0.5

*¹Water-soluble organic carbon.

*²Not determined.

fractions, respectively. The organic matter contents and pH in swine and cattle manure compost were 747 and 850 mg g⁻¹ and 8.0 and 6.9, respectively, and other chemical properties of compost have been reported previously [13]. Compost fractionation followed the method described by Katoh et al. [13]. Briefly, commercial swine manure compost was combusted at 600°C for 2 h. The residue after combustion was collected and used as the inorganic compost fraction. Commercial cattle manure compost was subjected to extraction with 1 M HCl (1:50 solid/liquid ratio) for 1 h to remove almost all the inorganic and acid-soluble organic fractions in the compost [24]. The residue after extraction was collected and used as the organic compost fraction.

After the fractionation, lead was sorbed on each fraction. The inorganic and organic fractions were added into polypropylene (PP) tubes containing 2 and 20 g-Pb/L, respectively, as Pb (NO₃)₂ in 5 mM KNO₃ (pH 5) at a 1:50 solid/liquid ratio. The fractions were then shaken for 24 h and pH was adjusted to 5. After centrifugation (5000 rpm, 5 min), the deposit was collected and washed five times with ultrapure water, and pH was adjusted to 7 using 0.001–0.1 M KOH, and the deposit was air-dried and passed through a 0.5 mm sieve. Table 2 shows selected chemical properties of the lead-sorbed fractions. The lead-sorbed inorganic and organic fractions were mixed at a ratio of 1:3, and the mixed sample was used as the lead-sorbed compost. The mixing ratio of the inorganic and organic fractions was a suitable ratio for lead immobilization [16] and was within the average values for Japanese AMC [25].

2.3. Plant Growth Test. A plant growth test was carried out in 15 mL PP tubes. The tube bottom was cut, and cotton was placed inside the bottom. The lead-sorbed compost was mixed well with the soil to give a final lead concentration of 1000 mg-Pb kg⁻¹, which corresponded to the ratio of 15.8 g of the lead-sorbed compost to one kg of soil. Into each tube was placed 12.5 g of soil, and seeds of buckwheat (*Fagopyrum esculentum*) or Guinea grass (*Panicum maximum* J.) were sown. Tubes without plants were also prepared as controls. In addition, plants were also grown in soil that did not contain the lead-sorbed compost. Three tubes were prepared for each treatment. After germination, the plants were thinned, and one plant per tube was grown for 3 months at 25°C (room temperature) with a 14 h photoperiod using a 40 W horticultural lamp. Ultrapure water containing 10 mg/L KNO₃ was irrigated from the bottom of the tube for 30 min to 1 h once every two days. After plant growth was

complete, the aboveground plant was cut, the plant height was measured, and then the shoot was dried and weighed. The total concentration of lead in the dried shoots was determined. The soil sample was collected from the tube. This study defined the entire soil sample collected from each tube as rhizosphere soil because the inside of the tubes was fully covered with plant roots. The collected soil samples were air-dried and passed through a 2 or 0.425 mm sieve before chemical analysis and lead release tests.

2.4. Lead Release Tests for Rhizosphere Soil. Following the period of plant growth, the kinetics of lead release from the rhizosphere soil containing lead-sorbed compost were investigated following the method described by Zhang and Ryan [26]. Briefly, a 1.0 g sample of the AMC-containing soil in which plants had been either grown or not grown was added to a beaker containing 1 L of 0.1 M NaNO₃ at pH 3, 4, 5, 6, or 7. The soil samples that had been passed through a 0.425 mm sieve were used. After the addition of the soil, stirring was started, while the pH of the sample was adjusted to ±0.2 of the target pH using 0.01 M NaOH or HNO₃. A 10 mL aliquot of the suspension was sampled at intervals of 1–90 min, passed through a 0.45 μm filter, and analyzed to determine the lead concentration using an inductively coupled plasma-atomic emission spectrometer (ICP-AES; ULTIMA2; HORIBA Ltd., Japan).

2.5. Analytical Methods. The pH and electrical conductivity (EC) of the soil samples were measured in ultrapure water with a solid/liquid ratio of 1:10 using a pH meter (MM-60R; DKK-TOA Co., Japan). The soil texture was determined using the hydrometer method [27]. The total carbon and total nitrogen (TC and TN, resp.) contents of the soil and compost fraction samples were determined using a carbon, hydrogen, and nitrogen (CHN) elemental analyzer (MT-6; Yanaco New Science Inc., Japan). Water-soluble organic carbon (WSOC) was extracted from the air-dried soil and compost fraction samples using ultrapure water at a solid/liquid ratio of 1:10 and analyzed using a total organic carbon (TOC) analyzer (TOC-VWS; Shimadzu Co., Japan). CaCl₂-soluble lead was extracted from the air-dried soil using 0.1 M CaCl₂ at a solid/liquid ratio of 1:10 and was analyzed using ICP-AES. Amorphous iron was extracted using Shuman's method [28]. The total elemental contents in the soil, plant shoot, and compost fraction samples were determined by acid digestion with HNO₃ and HCl using a microwave. A sequential extraction procedure was performed on the air-dried soil sample (0.425 mm) according to the procedure described by Tessier

TABLE 3: Shoot biomass of plant.

Plant	Treatment	Height (cm)	Dry weight (mg plant ⁻¹)	Pb concentration (μg g ⁻¹)
Buckwheat	Control	81.5 ± 6.6	268 ± 57	ND* ¹
	+Pb/compost	80.4 ± 1.6	355 ± 55	891 ± 274
<i>P</i> value		0.873	0.335	
Guinea grass	Control	36.2 ± 6.4	72 ± 25	ND
	+Pb/compost	11.5 ± 2.5	7 ± 2	151 ± 22
<i>P</i> value		0.023*	0.064	

*¹Not detected (<0.5 μg g⁻¹).

et al. [29]. In short, each fraction was extracted with 1 M MgCl₂ solution (exchangeable fraction), 1 M sodium acetate solution at pH 5 (carbonate fraction), 0.04 M NH₂OH-HCl in 25% (v/v) HOAc in a 95°C water bath with occasional agitation (Fe/Mn oxide fraction), 0.02 M HNO₃ and 5 mL 30% H₂O₂ solution in 85°C water bath with occasional agitation (organic fraction), and 5 mL HNO₃ and 2 mL HCl using a microwave oven (residual fraction). All the extracted and digested solutions were passed through a 0.45 μm filter and analyzed using ICP-AES to determine the elemental concentrations.

2.6. Statistical Analysis. Statistical analyses were performed using JMP Ver. 8.0.2 (SAS Institute Inc., USA). Analysis of variance (ANOVA) was conducted to compare the height and dry weight of plant shoots, soil pH, WSOC, and CaCl₂-soluble lead in the soil, as well as the percentage of lead dissolved in the dissolution test. The differences between the mean values were determined using Tukey's honestly significant difference (HSD) test at a 95% confidence level.

3. Results and Discussion

3.1. Plant Shoot Biomass. Table 3 shows the shoot biomass and lead concentration for plants grown in the rhizosphere soil with or without the lead-immobilized compost. The shoot height and dry weight of buckwheat grown in the presence of lead-immobilized compost did not significantly differ from those grown without the compost. However, the lead concentration in buckwheat grown in the presence of lead-immobilized compost was relatively high at 891 μg g⁻¹. Buckwheat is known to tolerate high levels of lead and to act as a lead hyperaccumulator, which is defined as a plant containing over 1000 μg g⁻¹ of lead in its shoots [30]. Therefore, in the rhizosphere soil containing lead-immobilized compost, plant growth was not suppressed by lead toxicity, despite the fact that lead was absorbed by the buckwheat root. In contrast, the presence of lead-immobilized compost led to growth suppression in Guinea grass, as this species is known to exhibit lower lead tolerance [31].

In both plant types, lead was absorbed from the rhizosphere soil, even though the lead in the soil was immobilized and insoluble, suggesting that rhizosphere effects had altered the immobilized lead to increase bioavailability. In the bulk lead-contaminated soil amended with the AMC, lead uptake

TABLE 4: Rhizosphere soil pH for buckwheat, Guinea grass, and bulk soil (no plant).

Plant	Treatment	Soil pH
Buckwheat	No Pb	5.6 ± 0.0 ^{C*1}
	Pb-compost	6.1 ± 0.0 ^B
Guinea grass	No Pb	6.9 ± 0.0 ^A
	Pb-compost	6.8 ± 0.0 ^A
No plant		6.8 ± 0.0 ^A

*¹Different letters indicate significant differences at *P* < 0.05 on the basis of Tukey's HSD test.

is suppressed at the same level as the inorganic immobilization material [15]. According to Katoh et al. [32], in the rhizosphere soil amended with hydroxyapatite, which is the main component of the inorganic compost fraction used in this study [13], lead was not absorbed by the plant root. This is because lead is immobilized by hydroxyapatite, mainly precipitating as pyromorphite, which has a low solubility product (log *K*_{sp} = -25.05 [14]). In addition, in this study, the lead concentration in buckwheat (891 μg g⁻¹) was lower than that previously reported (4200 μg g⁻¹ [30]), which suggests that a large part of the lead immobilized by the inorganic compost component was not altered by rhizosphere effects to be bioavailable. Therefore, lead uptake by both plants would be best explained by partial lead release from the lead-immobilized organic fraction in the compost. The lead release from the lead-immobilized organic fraction in the compost is discussed in detail in the later section relating to the lead phases in the soil.

3.2. Soil pH, Water-Soluble Organic Carbon (WSOC), CaCl₂-Soluble Lead, and Lead Phases. The pH of the buckwheat rhizosphere soil with and without the lead-immobilized compost was 5.6 and 6.1, respectively, which was significantly lower than that of the Guinea grass rhizosphere soil and the nonplanted soil (Table 4), indicating that the rhizosphere effect of buckwheat caused the pH reduction.

The level of WSOC in the rhizosphere soil of buckwheat was significantly higher than that in the nonplanted soil (Figure 1(a)), while the level of WSOC in the rhizosphere soil of Guinea grass was higher but not significantly different from that in the nonplanted soil. The higher level of WSOC in the buckwheat rhizosphere soil would be attributed to

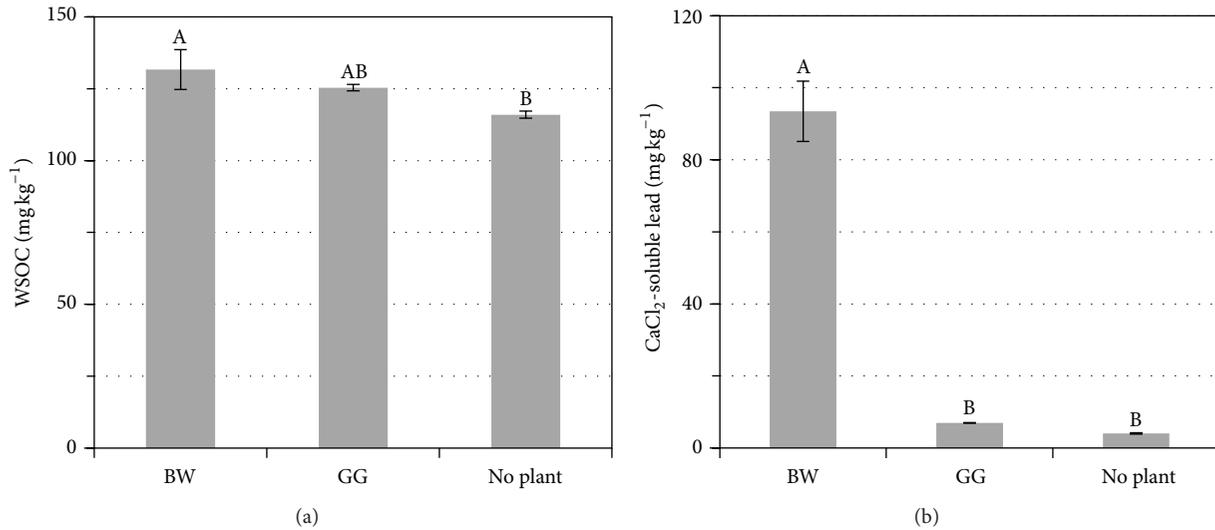


FIGURE 1: (a) Water-soluble organic carbon (WSOC) and (b) CaCl₂-soluble lead in the rhizosphere soil of buckwheat (BW) and Guinea grass (GG) and bulk soil (no plant) containing lead-sorbed compost. Bars indicate the standard error (SE) (*n* = 3). Different letters indicate significant differences at *P* < 0.05 based on Tukey’s HSD test.

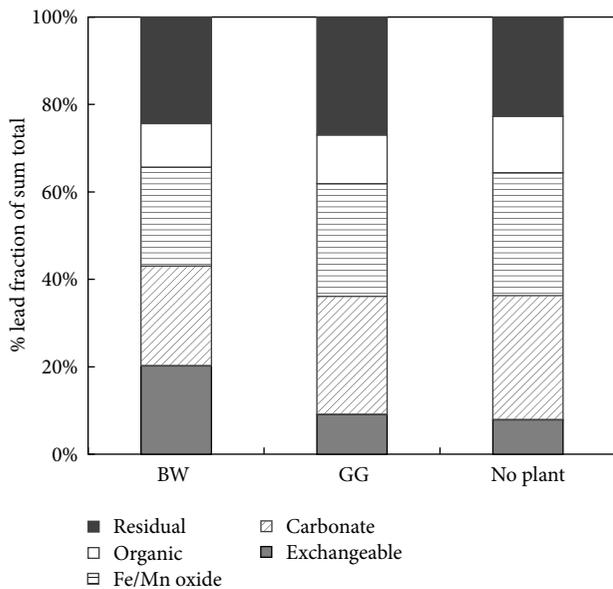


FIGURE 2: Sequential extraction of lead from the rhizosphere soil of buckwheat (BW) and Guinea grass (GG) and bulk soil (no plant) containing lead-sorbed compost.

both the release of water-soluble organic matter from the root and decomposition of the organic fraction of the compost. The amount of CaCl₂-soluble lead in the rhizosphere soil of buckwheat was significantly higher than that present in the rhizosphere soil of Guinea grass and nonplanted soil (Figure 1(b)). The amount of CaCl₂-soluble lead in the rhizosphere soil of Guinea grass was slightly higher than that in the nonplanted soil but was not significantly different.

Figure 2 shows the lead fractions recorded in sequential extractions. The average recovery, which is defined in this study as the ratio of the sum total level of each fraction

(Figure 2) to the total level of lead in the soil (1000 mg kg⁻¹), was 93 ± 6%. The ratio of each fraction in the nonplanted soil containing the lead-sorbed compost was 8% for the exchangeable fraction, 28% for the carbonate fraction, 28% for the Fe/Mn oxide fraction, 13% for the organic fraction, and 23% for the residual fraction, demonstrating that 36% of lead in the soil (exchangeable and carbonate fractions) was present in relatively soluble states. According to other studies [15, 16], wherein the lead distribution by sequential extraction was investigated using the lead-contaminated soil amended with the AMC, the residual and exchangeable fractions ranged from 17% to 49% and from 0% to 1%, respectively. The residual and exchangeable lead fractions in this study were compatible with those previously reported, although the lead-immobilized compost was applied to the noncontaminated soil in this study. In addition, the application of organic waste material to the contaminated soil alters the lead phases to more insoluble state [33, 34]. The distribution of each fraction, particularly the exchangeable and carbonate fractions, in the rhizosphere soil of Guinea grass was almost the same as that in the nonplanted soil, suggesting that the growth of Guinea grass did not influence the lead phases in the rhizosphere soil containing the lead-immobilized compost. In contrast, the exchangeable fraction made up 20% of the lead in the rhizosphere soil of buckwheat, while the ratios of carbonate and Fe/Mn oxide fractions decreased as compared with the nonplanted soil. These results indicate that the growth of buckwheat caused an increase in the amount of exchangeable lead in the rhizosphere soil containing lead-sorbed compost.

The chemical and biological properties of the rhizosphere soil differ considerably from those of the nonplanted soil because of root exudation, which changes the redox potential, microbial activities, biomass, and the chemical speciation of elements [18]. In the rhizosphere soil of buckwheat, the pH

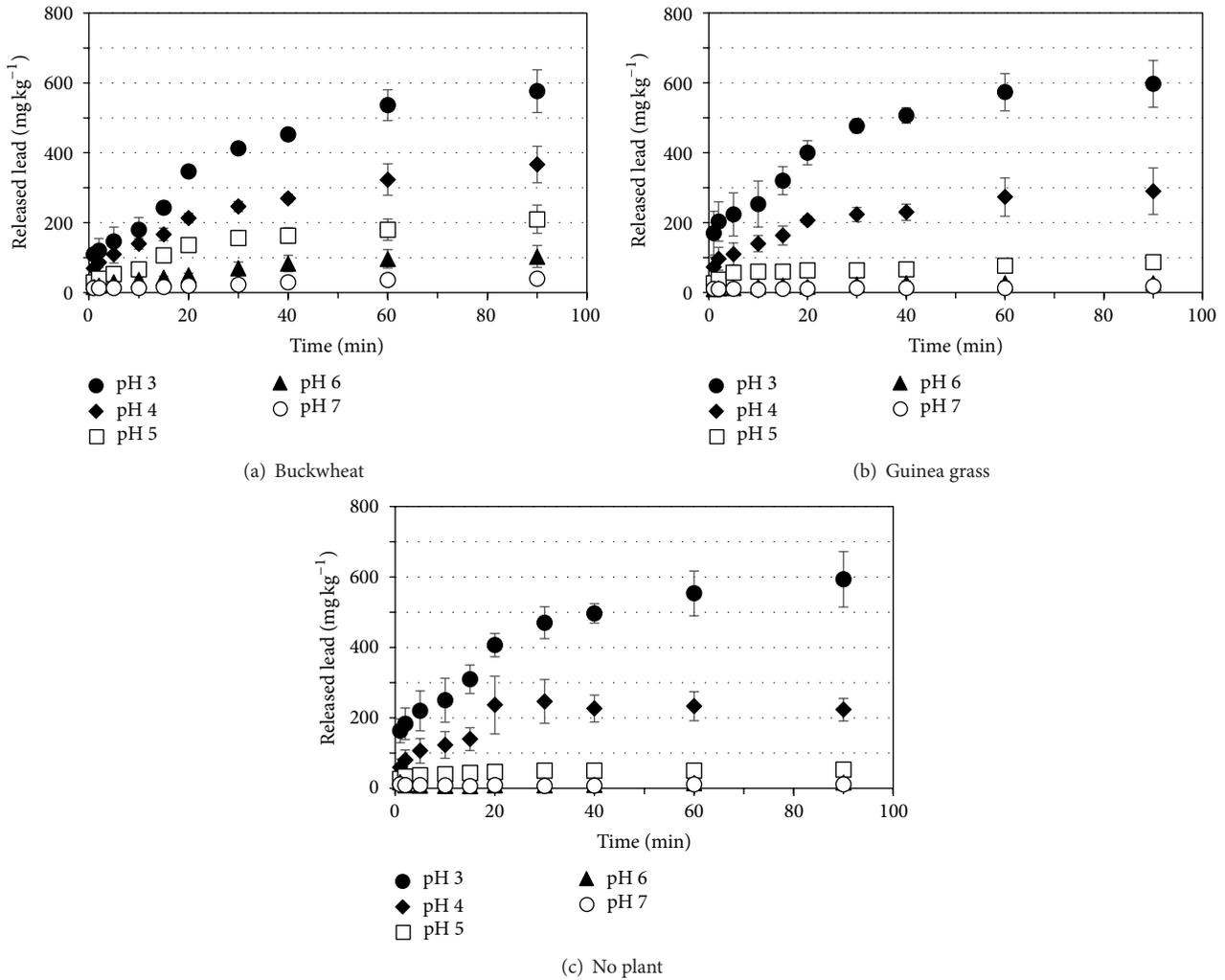


FIGURE 3: Lead release from rhizosphere soil of buckwheat and Guinea grass and bulk soil (no plant) with lead-sorbed compost. Bars indicate the SE ($n = 3$).

decreased compared with that of the nonplanted soil. In addition, the level of WSOC in the rhizosphere soil of buckwheat was significantly higher than that in the nonplanted soil. Therefore, such changes in the rhizosphere soil of buckwheat would induce the lead immobilized on the compost to become more soluble; the ratio of the exchangeable fraction increased, resulting in the observed enhancement in the level of CaCl_2 -soluble lead. As discussed in the previous section, lead immobilized by the inorganic fraction of the compost is relatively stable with regard to chemical and biological changes in the soil. Thus, lead immobilized by the organic fraction in the compost would be responsible for the increase in the exchangeable fraction in the sequential extractions and the level of CaCl_2 -soluble lead. Lead is sorbed onto organic matter by complexation with surface functional groups such as carboxyl groups [12]; a pH decrease then causes lead sorbed onto the organic matter to be released [12, 35]. In addition, lead-sorbed organic matter is redistributed by the decomposition of the organic matter to which the lead is sorbed [19]. Therefore, in the rhizosphere soil of buckwheat, the high rhizosphere effect might induce a pH decrease and

an enhancement in the microbial decomposition of organic matter as a result of the high level of water-soluble organic matter, causing the lead to be released from the organic fraction in the compost. In contrast, in the rhizosphere soil of Guinea grass, the relatively low rhizosphere effect would explain the absence of a significant enhancement in the level of CaCl_2 -soluble lead and the lack of change in the distribution of each fraction in the sequential extractions.

3.3. Lead Release from Rhizosphere Soil. Figure 3 shows the lead released from the rhizosphere soil of buckwheat and Guinea grass and nonplanted soil containing lead-immobilized compost as a function of contact time. The amount of lead released increased with an increase in time for all the soils and solution pHs. In addition, for the same soil, a decrease in the solution pH resulted in an increase in the amount of lead released. With the exception of pH 3, it may be seen that the amount of lead released at a specific pH followed the order rhizosphere soil of buckwheat > rhizosphere soil of Guinea grass = nonplanted soil. Table 5 shows the percentage

TABLE 5: Lead released after 90 min as a percentage of the total lead content in soil.

Plant	Solution pH				
	3	4	5	6	7
Buckwheat	58 ± 6	37 ± 5	21 ± 4 ^{A*1}	10 ± 3 ^A	4 ± 1 ^A
Guinea grass	60 ± 7	29 ± 7	9 ± 0 ^B	3 ± 1 ^{AB}	2 ± 0 ^B
No plant	59 ± 8	22 ± 3	5 ± 0 ^B	2 ± 0 ^B	1 ± 0 ^B

*1 Different letters in the same column indicate significant differences at $P < 0.05$ on the basis of Tukey's HSD test.

of lead released at 90 min as a percentage of the total lead content (1000 mg kg^{-1}) in the soil. At pH 3, 58%–60% of the lead in the soil was released, and no significant differences between the soils were observed. In the rhizosphere soil of Guinea grass and nonplanted soil, the percentages of lead released decreased with an increase in the solution pH, and the values were not significantly different between the two soils. Similarly, in the rhizosphere soil of buckwheat, the percentages of lead released decreased with an increase in the solution pH, but they were significantly higher than those in the rhizosphere soil of Guinea grass and nonplanted soil when the solution pH was between 5 and 7. To assess the release rates and initial release rates, the kinetics data were analyzed according to the pseudo-second-order rate equation given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (1)$$

where k_2 is the pseudo-second-order rate constant ($\text{kg} (\text{mg min})^{-1}$), q_e and q_t are the amounts of lead released (mg kg^{-1}) at equilibrium and at time t , respectively, and t is contact time (min). The following expression denotes the initial release rate ($\text{mg} (\text{kg min})^{-1}$):

$$h = k_2 q_e^2. \quad (2)$$

The results obtained from the analyses are shown in Table 6. The data were fitted well by the pseudo-second-order kinetics model with a high determination coefficient, and the amounts of lead released at equilibrium were estimated, which increased with a decrease in the solution pH within the same soil. Similarly, the initial release rates were assessed. Similarly, the initial release rate increased with a decrease in the solution pH within the same soil.

At pH 5–7, higher levels of compost-immobilized lead were released into the rhizosphere soil of buckwheat than in nonplanted soil; there was no significant difference between the lead levels found in the rhizosphere soil of Guinea grass and nonplanted soil. These results were consistent with the results of the lead bioavailability screening and the phase analysis described in Section 3.2. According to the results of the sequential extractions (Figure 2), the exchangeable, carbonate, and Fe/Mn oxide fractions in the rhizosphere soil of buckwheat and Guinea grass and nonplanted soil represented 66%, 62%, and 64%, respectively, of the sum total of lead recovered, which corresponded to the percentage of lead released after 90 min at pH 3 (Table 5). Similarly, the sum

percentages of exchangeable and carbonate fractions were 43%, 36%, and 36%, respectively; these values were larger than the percentages of lead released at pH 4. These results suggest that lead immobilized by the compost was released from the exchangeable, carbonate, and Fe/Mn oxide fractions at pH 3 and from the exchangeable fraction and a part of carbonate fraction at pH 4. Thus, small differences in the distribution of the exchangeable to Fe/Mn oxide fractions would explain the absence of significant differences in the amount of lead released for each soil type at both pH 3 and pH 4. The exchangeable fraction in the rhizosphere soil of buckwheat and Guinea grass and nonplanted soil represented 20%, 9%, and 8%, respectively, of the total lead recovered, and these values were almost equal to the percentage of lead released in the lead release test at pH 5. This suggests that the lead that was released was derived from the exchangeable fraction in the rhizosphere soils and nonplanted soil at pH 5–7. Therefore, the differences between the percentage of exchangeable lead present in the rhizosphere soil of buckwheat and other soils would be responsible for the significant differences in the amount of lead released in the lead release test at pH 5–7. These results suggest that the rhizosphere effect induces an increase in the percentage of lead present in the exchangeable phase and leads to the remobilization of AMC-sorbed lead. Therefore, AMC should be applied to soils that contain plants that are unable to alter the lead phases present in the shooting range soil. In particular, efforts should be made to ensure that lead cannot be transformed to the exchangeable phase when AMC is used as an immobilization material in the shooting range soil. However, lead uptake and suppression of plant growth was observed in Guinea grass, despite the fact that lead was not remobilized in the rhizosphere soil. This observation would imply that even miniscule changes in lead bioavailability resulting from a weak rhizosphere effect could be enough to cause an increase in lead uptake by plants. Therefore, it should also be noted that even plants with a low potential to remobilize lead may take up lead immobilized by AMC, even though that lead is not released from the rhizosphere soil to the nonrhizosphere soil.

4. Conclusions

The shoot height and dry weight of buckwheat grown in rhizosphere soil of shooting range with lead-immobilized compost did not significantly differ from that grown without compost, while the presence of lead suppressed the growth of Guinea grass. In both plant types, lead was absorbed from the rhizosphere soil although the lead had been immobilized by the compost. The presence of buckwheat in the rhizosphere soil caused a reduction in the rhizosphere soil pH and an increase in the level of WSOC compared with that in nonplanted soil. In addition, the presence of buckwheat altered the lead phases present; the relative amount of the soluble exchangeable fraction increased, resulting in an increase in the CaCl_2 -soluble lead level. In contrast, the presence of Guinea grass did not significantly change the lead bioavailability or the phases present.

TABLE 6: Computed values of the pseudo-second-order rate constant (k_2) and initial lead dissolution rate (h).

Plant	pH	q_{eq} (mg kg^{-1})	k_2 (kg (mg min)^{-1}) ($\times 10^{-4}$)	R^2	h (mg (kg min)^{-1})
Buckwheat	3	670	0.870	0.948	39
	4	402	1.72	0.962	28
	5	236	2.73	0.968	15
	6	120	4.70	0.944	7
	7	44	14.2	0.913	3
Guinea grass	3	651	1.55	0.979	66
	4	309	3.53	0.984	34
	5	86	21.0	0.982	16
	6	28	61.0	0.986	5
	7	17	79.9	0.944	2
No plant	3	643	1.53	0.979	64
	4	244	8.47	0.982	50
	5	54	74.1	0.998	21
	6	17	42.7	0.847	1
	7	11	149	0.934	2

The lead release test in solution using the rhizosphere soil showed that lead immobilized by the compost was released more easily from the soil at low solution pH, regardless of the soil types. Between solution pH 5 and solution pH 7, the amount of lead released from the compost was higher in the rhizosphere soil of buckwheat than in the nonplanted soil, whereas there was no significant difference between the rhizosphere soil of Guinea grass and nonplanted soil. The lead released from the rhizosphere soil between solution pH 5 and solution pH 7 would be derived from the exchangeable lead form. These results suggest that the increase in the quantity of exchangeable lead resulting from the rhizosphere effect induces lead immobilized by the AMC to be remobilized. Therefore, AMC should be applied to soils that contain plants that are unable to alter the lead phases present in the shooting range soil. In particular, efforts should be made to ensure that lead cannot be transformed to the exchangeable phase. However, it should be also noted that even plants with a low potential to remobilize lead may take up lead immobilized by AMC from the rhizosphere soil of shooting range.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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