JARQ 47 (3), 273 – 281 (2013) http://www.jircas.affrc.go.jp

Remediation of Cadmium-contaminated Paddy Soils by Washing with Ferric Chloride ($FeCl_3$): Effect of Soil Washing on the Cadmium Concentration in Soil Solution and Spinach

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Abstract

We evaluated the effects of soil washing with ferric chloride ($FeCl_3$) on cadmium (Cd) concentrations in soil solutions and Cd absorption by two spinach cultivars in pot experiments. Soil samples were collected from washed and unwashed plots of rice paddy fields in Fukuoka and Toyama, Japan. Spinach pot cultivation was performed with the above mentioned soil under oxidative conditions. Before and after spinach cultivation, the Cd content in washed soils was always lower than that in unwashed soils. Soil washing with $FeCl_3$ affected the exchangeable cations (i.e. calcium increased and magnesium decreased). The Cd concentration in the soil solution from washed plot was lower than that in the solution from the unwashed plot throughout the spinach growth period, which was attributed to the exchangeable Cd content in both soils, because the fraction equilibrated with the Cd concentration in the soil solution. The exchangeable cation composition was affected by soil washing, but no significant difference in spinach yield was observed between the washed and unwashed plots. The leaf Cd concentration in the two spinach cultivars was up to 70% lower in the washed soils. This study suggested that soil washing in rice paddy fields with $FeCl_3$ was effective for controlling the Cd absorption risk of upland crops such as spinach. However, some risks remain to clear the CODEX standard (0.2 mg kg^{-1}) in the Cd content of leaf such as spinach, which has a high Cd absorptive capacity.

Discipline: Agricultural environment
Additional key words: chemical washing, heavy metal, leaf vegetable, pot experiment, remediation technology

Introduction

In Japan, cadmium (Cd) pollution in agricultural soil has been a serious problem since the 1960s. There are 532 working mines, including 53 metal mines in Japan[16]. Mine wastewater from metal factories often mixed with agricultural water before flowing into rice paddy fields[20]. The Agricultural Land Soil Pollution Prevention Law was enacted to designate a certain amount of land as pollution-free and suitable for agricultural use[17]. Although the Agricultural Land with Soil Pollution Control covered 6428 ha, Cd pollution mitigation measures were completed inapproximately 90% of this land by the end of 2010 fiscal year[19]. The standard limit for the Cd concentration in brown rice was set at 0.4 mg kg^{-1} by the Codex Alimentarius Commission of the FAO and WHO[4]. In response, the standard value for the Cd content of rice in Japan declined to 0.4 from 1 mg kg^{-1} [18], hence the need to develop promising technologies to reduce Cd concentration in crops.

Several remedial technologies have been proposed to treat Cd-contaminated soil including soil dressing, water

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Received 5 September 2012; accepted 13 November 2012.

management (for rice paddy fields), chemical cleaning of the soil, phytoextraction, and the use of rootstock varieties[1]. Soil washing with chemicals can remove Cd from contaminated soil swiftly and effectively[5]. However, soil washing methods based on $CaCl_2$ can affect soil fertility, although they reduce the Cd content of brown rice to the standard value (0.4 mg kg^{-1} Cd) [4] or less[11]. Maejima et al.[9] conducted pot experiments with soybeans using washed soils sampled from Nagano Prefecture in Japan. They reported that the Cd content of two soybean cultivars was reduced in the washed soils compared with the unwashed soils. Makino et al.[12] previously used ferric chloride ($FeCl_3$) as a suitable chemical to remedy Cd-contaminated paddy soil and established optimal washing conditions for efficient and environmentally-friendly chemical remedying of Cd-contaminated rice paddy fields[12]. Makino et al.[13] also confirmed the effects of soil washing using $FeCl_3$ in an on-site scale experiment in Cd-contaminated paddy fields. Although this method could be widely used, the effects of soil washing with $FeCl_3$ on various soil properties, such as pH, electrical conductivity (EC), exchangeable cations, and the growth of upland crops must be investigated.

The average order of Cd accumulation by vegetable species is as follows: leafy vegetables > solanaceous vegetables > kale vegetables > root vegetables > alliums > melon vegetables > legumes[27]. Accordingly, spinach may be expected to more readily take up and accumulate Cd from the soil[21]. Although the standard Cd value of leafy vegetables was set at 0.2 mg kg^{-1} FW[3], 3% of the total harvested spinach exceeds this level in Japan[14]. This means some leafy vegetables produced in Japan, including spinach, are likely to exceed the standard value.

The objectives of the present study were to examine the effects of soil washing using $FeCl_3$ on upland soils and the washing effect on spinach representing leafy vegetables.

Materials and methods

1. Soil

Soil samples were collected from the Ap horizon in paddy fields in Fukuoka and Toyama Prefectures, Japan, where on-site soil washing was performed. Paddy fields were located in the Cd pollution measure area where brown rice may be produced exceeding the Cd standard value (0.4 mg kg^{-1}). The on-site soil washing procedure was conducted as follows. Cd-contaminated paddy fields were washed chemically with $FeCl_3$ to extract Cd from the soil. For water wash, slurry and agricultural water were mixed to remove any residual Cd and chlorine (Cl^-). Wastewater was processed by an on-site wastewater treatment system employing a coagulation-sedimentation method with chelating agent treatment to collect and remove Cd from the wastewater[11,25]. The complete details of the $FeCl_3$ soil washing method and Cd extraction mechanism were reported by Makino et al.[12].

After on-site soil washing, rice plants were transplanted into chemically washed plots in each field and unwashed control plots. After rice cultivation, soil samples from the washed and unwashed plots were collected for a pot culture experiment. The Cd concentrations of unwashed and washed soils in the Fukuoka fields (extracted with 0.1 M HCl) before spinach cultivation were 2.42 and 0.68 mg kg^{-1} (Table 1), respectively, indicating removal efficiency of approximately 72%. The soil Cd concentration (extracted with 0.1 M HCl) of the unwashed and washed soils in the Toyama fields before spinach cultivation were 0.22 and 0.08 mg kg^{-1} (Table 2), respectively, indicating removal efficiency of approximately 64%. The Fukuoka soil was classified as a Hydraquent[26] and the texture was a clay loam (ratio of sand to silt and clay = 52.2:23.1:24.7). The Toyama soil was an Epiaquent[24] and the texture was a sandy loam (ratio

Table 1. Comparison of the soil properties between unwashed and $FeCl_3$-washed soils from Fukuoka

Soil treatment	pH		EC	Exchangeable cations (cmolc kg^{-1})				Soil Cd (mg kg^{-1})		
	(H_2O)	(KCl)	(S m^{-1})	Ca^{2+}	Mg^{2+}	K^+	Na^+	Exchangeable[a]	Weak acid soluble[b]	Acid soluble[c]
Before cultivation										
Unwashed	5.73±0.01	4.07±0.00	0.03±0.00	8.38±0.17	1.24±0.02	0.50±0.01	0.35±0.01	0.16±0.00	0.53±0.01	2.42±0.03
Washed	5.39±0.01	4.50±0.01	0.30±0.00	10.15±0.22	0.70±0.01	0.42±0.01	0.36±0.01	0.05±0.00	0.15±0.01	0.68±0.01
After cultivation "Active"										
Unwashed	5.66±0.02	4.86±0.01	0.42±0.02	9.55±0.34	1.83±0.07	0.76±0.04	0.47±0.02	0.10±0.03	0.36±0.01	2.30±0.07
Washed	5.62±0.05	4.90±0.03	0.53±0.04	12.44±0.24	1.30±0.03	0.62±0.03	0.48±0.00	0.02±0.01	0.08±0.00	0.70±0.01
After cultivation "Banchu Palk"										
Unwashed	5.64±0.04	4.85±0.01	0.43±0.03	9.62±0.12	1.81±0.02	0.75±0.03	0.47±0.01	0.08±0.00	0.34±0.02	2.31±0.06
Washed	5.63±0.04	4.90±0.01	0.54±0.05	12.77±0.34	1.34±0.05	0.67±0.04	0.49±0.01	0.03±0.01	0.08±0.00	0.70±0.02

a, b and c are 1 M NH_4NO_3, 0.01 M HCl, and 0.1 M HCl, respectively.
Mean values are showed with standard deviation (n = 3)

Table 2. Comparison of the soil properties between unwashed and $FeCl_3$-washed soils from Toyama

Soil treatment	pH		EC	Exchangeable cations (cmolc kg^{-1})				Soil Cd (mg kg^{-1})		
	(H_2O)	(KCl)	(S m^{-1})	Ca^{2+}	Mg^{2+}	K^+	Na^+	Exchangeable[a]	Weak acid soluble[b]	Acid soluble[c]
Before cultivation										
Unwashed	5.29±0.01	4.03±0.00	0.05±0.00	2.03±0.04	1.26±0.02	0.44±0.02	0.20±0.01	0.04±0.00	0.14±0.01	0.22±0.01
Washed	5.33±0.01	4.07±0.01	0.07±0.03	3.22±0.04	0.51±0.02	0.33±0.01	0.21±0.01	0.01±0.00	0.06±0.02	0.08±0.01
After cultivation "Active"										
Unwashed	5.02±0.02	4.37±0.03	0.67±0.09	6.82±0.27	1.07±0.04	0.64±0.04	0.27±0.01	0.02±0.00	0.11±0.01	0.24±0.01
Washed	5.09±0.03	4.41±0.02	0.64±0.08	7.35±0.36	0.81±0.01	0.52±0.03	0.28±0.02	0.01±0.00	0.05±0.00	0.10±0.01
After cultivation "Banchu Palk"										
Unwashed	5.06±0.02	4.41±0.03	0.63±0.02	6.90±0.36	1.08±0.02	0.59±0.01	0.28±0.01	0.02±0.00	0.11±0.00	0.23±0.02
Washed	5.11±0.01	4.41±0.01	0.66±0.10	7.39±0.28	0.82±0.01	0.50±0.01	0.29±0.01	0.01±0.00	0.05±0.00	0.11±0.01

a, b and c are 1 M NH_4NO_3, 0.01 M HCl, and 0.1 M HCl, respectively.
Mean values are showed with standard deviation (n = 3)

of sand to silt and clay = 73.9:16.7:9.4). The general physicochemical properties of the Fukuoka and Toyama soils were reported by Ibaraki et al.[7] and Makino et al.[10], respectively.

2. Pot culture experiments

The fresh soil samples were passed through an 8-mm mesh sieve. Approximately 5.5 kg of each fresh soil sample (4 kg on an oven-dried soil basis) was placed in 5 L plastic pots and two spinach cultivars were planted in the pots (i.e. Active and Banchu Palk). For the Fukuoka soil, a basal fertilizer application was supplied containing 0.54 g of nitrogen (N), 0.20 g of phosphorus (P), and 0.45 g of potassium (K) per pot, as urea [$(NH_4)_2CO$], superphosphate, and potassium chloride (KCl), respectively. The superphosphate was a mixture of monocalcium phosphate [$Ca(H_2PO_4)_2 \cdot H_2O$] and calcium sulfate ($CaSO_4$). For the Toyama soil, a basal fertilizer application was supplied containing 0.36 g of N, 0.92 g of P, and 0.36 g of K per pot as $(NH_4)_2CO$, superphosphate, and KCl, respectively. Calcium carbonate ($CaCO_3$) was added to each fresh soil sample to adjust the soil pH to 6. Five seeds were sown directly into each pot and the seedlings of each cultivar were thinned out to three per pot at 10 d after sowing. The spinach leaves were harvested at 36 d after sowing. The soil moisture content was maintained at approximately 60–70% of the maximum water-holding capacity throughout the growth period. This pot experiment was conducted in triplicate in a greenhouse under temperature-controlled conditions (25°C).

3. Soil analysis

Before and after spinach cultivation, soil samples were air-dried and passed through a 2-mm mesh sieve for analysis. The pH (H_2O or KCl) was measured (soil: solution = 1:2.5) using a pH meter with a glass electrode (UB-10, Denver Instrument Co., Arvada, CO, USA). EC was measured (soil: solution = 1:5) using an EC meter (MC126, Mettler-Toledo K.K., Columbus, OH, USA). Different forms of soil Cd were determined as described by Makino et al.[10]. Three extractants, 1 M ammonium nitrate (NH_4NO_3, pH 7.0), 0.01 M HCl, and 0.1 M HCl, were used for extraction. Cd concentrations were determined in each extract using inductively coupled plasma optimal emission spectrometry (ICP-OES, Vista-Pro, Varian, Palo Alto, CA, USA). The exchangeable cations in 1 M NH_4NO_3, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), K^+, and sodium (Na^+), were also determined by ICP-OES.

4. Soil solution

During the pot cultivation period, soil solutions were collected from the pots at a depth of 10 cm using ceramic porous cups (DIK-8391, Daiki Rika Kogyo Co., Ltd., Saitama, Japan). The soil solutions were filtered through a 0.2-μm membrane filter (Millex, Millipore Co., Billerica, MA, USA) and the concentrations of Cd^{2+} and major cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) in the filtrates were determined by ICP-OES. The anions (Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{2-}) were measured by ion chromatography (DX-320, Dionex Co., Sunnyvale, CA, USA). The pH of the filtrates was measured using a pH meter and the EC was measured using an EC meter.

5. Plant analysis

Spinach leaves were harvested from the washed and unwashed plots at 36 d after sowing. The leaves were oven-dried at 70°C for 24 h, ground to a fine powder using a stainless steel grinder (P-14, Fritsch, Idar-Oberstein, Germany) and used for plant analysis. One gram of each plant sample was digested with 5 mL of approximately 13.4 M nitric acid followed by 10 mL of 9.4 M perchloric acid, as described previously[11]. The Cd concentrations in the digested solutions were determined by ICP-OES.

Results and discussion

1. Comparison of Cd concentrations and exchangeable cations between $FeCl_3$-washed and unwashed soils

Tables 1 and 2 show the soil properties of washed and unwashed soils before and after spinach cultivation. The 1 M NH_4NO_3, 0.01 M HCl, and 0.1 M HCl-extracted Cd levels were used to evaluate the exchangeable, weak acid-soluble, and acid-soluble Cd, respectively. Before and after cultivation, the three forms of Cd were significantly lower in washed than unwashed soils (Tables 1 and 2). This result suggested that the effect of soil washing on Cd concentrations in rice paddy fields was maintained after conversion to upland farming. The pH (H_2O) levels of the Fukuoka and Toyama soils after spinach cultivation were lower than those before cultivation (Tables 1 and 2). However, the EC levels of the Fukuoka and Toyama soils were higher after spinach cultivation than those before cultivation. Spinach cultivation requires a greater application of chemical fertilizers compared with paddy rice cultivation. The nitrogen fertilizer urea causes acidification and increases the ionic strength of soils through nitrification. The high EC levels were also attributable to the application of $Ca(H_2PO_4)_2 \cdot H_2O$ and KCl. The exchangeable cation concentrations of the washed Fukuoka and Toyama soils differed from those of the unwashed soils (Tables 1 and 2). The increase in Ca^{2+} was attributable to the application of $CaCO_3$, which was used to neutralize the soil pH after $FeCl_3$ washing. Soil washing with $FeCl_3$ affected the composition of the exchangeable cations, particularly decreasing Mg^{2+} and K^+ levels.

2. Cd concentrations in soil solution throughout the spinach growth season

Figure 1 shows Cd concentrations in soil solution throughout the spinach growth season. Cd concentrations were lower in washed than unwashed soils during the growth season (Fig. 1). In the Fukuoka soil (Fig. 1a), the maximum Cd concentration in soil solution was recorded at 9 d after sowing, and the Cd levels in the washed and unwashed plots were 5.3–5.9 and 21.7–23.3 µg L^{-1}, respectively. The lowest Cd concentration in soil solution was detected at 36 d after sowing, and the Cd levels in the washed and unwashed plots were 0.8–1.1 and 3.9–4.5 µg L^{-1}, respectively, which showed that Cd levels were effectively reduced by two-thirds after soil washing. In the Toyama soils (Fig. 1b), the lowest Cd concentration in soil solution was detected at 8 d after sowing, and the Cd concentrations of the washed and unwashed plots were 1.5–1.8 and 6.4–6.7 µg L^{-1}, respectively. The maximum Cd concentration was recorded at 22 d after sowing, and the Cd levels in the washed and unwashed plots were 5.4–5.8 and 15.0–16.4 µg L^{-1}, respectively. Thus, Cd concentrations in soil solution of unwashed soil always exceeded those in washed soils.

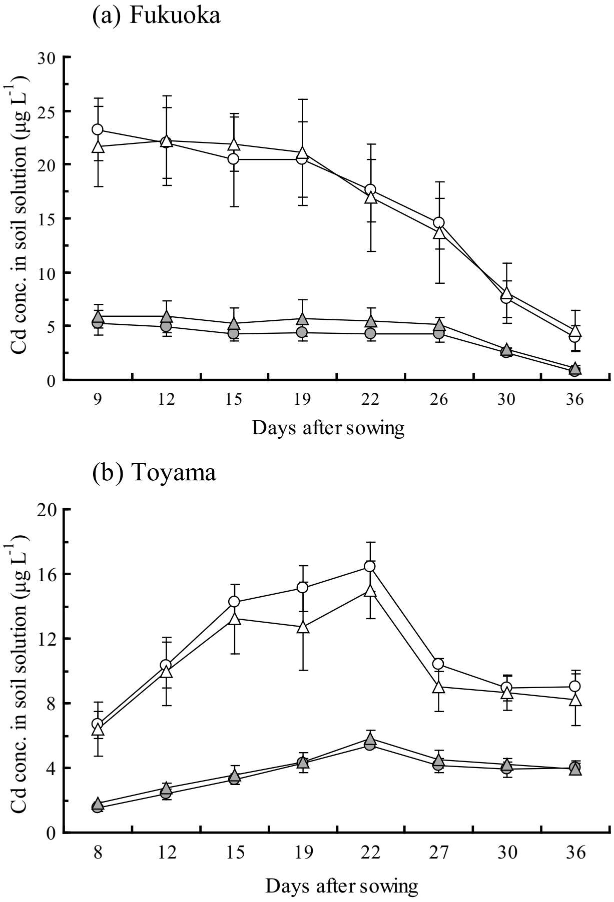

Fig. 1. Changes in cadmium (Cd) concentrations of soil solutions during pot growth experiments in (a) Fukuoka and (b) Toyama

Error bars indicate standard deviations (n = 3).
A, Active; BP, Banchu Palk.
–○– : Unwashed (A), –△– : Unwashed (BP),
–●– : Washed (A), –▲– : Washed (BP)

The Cd present in soil solution is usually considered to be the fraction that is most available to plants grown in Cd-containing soil, meaning the factors that control the release of Cd from soil must be considered. Soil pH is the key factor that affects the solubility of Cd in soil solution[8] under oxidized conditions. In this study, a significant correlation was found between pH and Cd in soil solution (Figs. 2a and 3a). The Cd concentrations in soil solution from washed soils were also relatively lower than those from unwashed soils, although the pH values were in the same range. This may be because the concentration of Cd in the soil, particularly exchangeable Cd, was low in the washed plot.

In contrast, the Cd concentration in soil solution rose with increasing EC, while the Cd concentration in soil solution from washed soils was relatively lower than that of unwashed soil with the same range of EC values (Figs. 2b

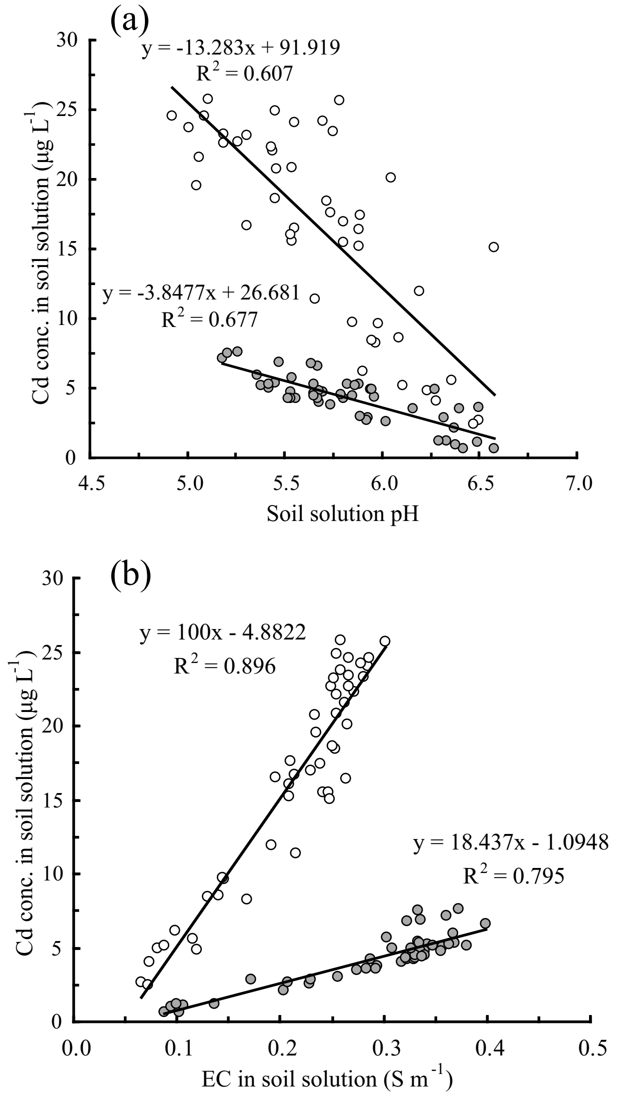

Fig. 2. Relationships between (a) pH and Cd concentrations and (b) electrical conductivity (EC) and Cd concentrations in Fukuoka soil solutions

○ : Unwashed, ● : Washed.

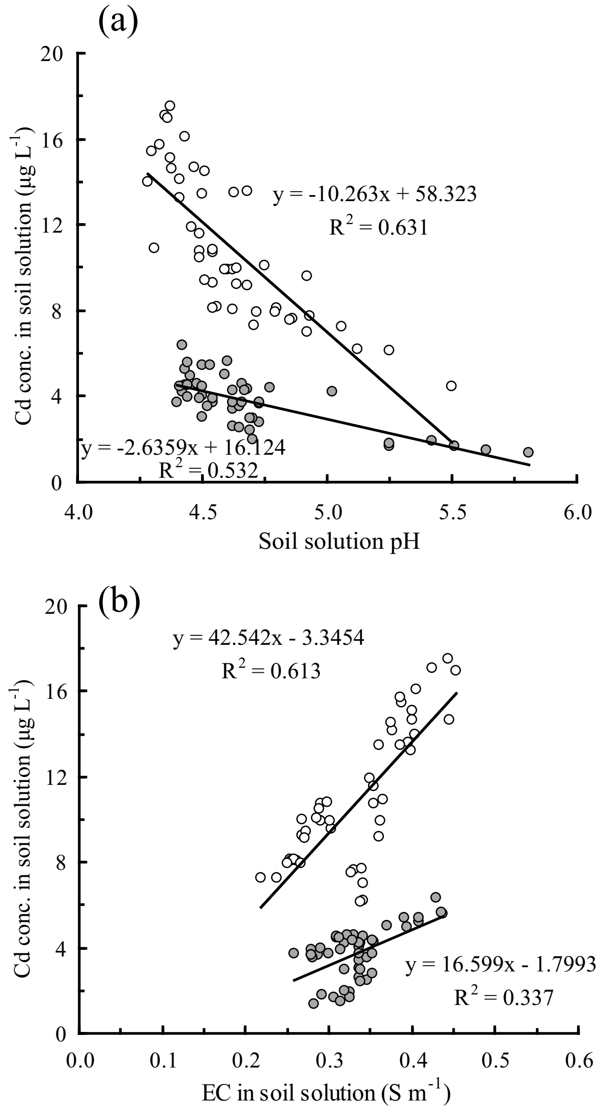

Fig. 3. Relationships between (a) pH and cadmium (Cd) concentrations and (b) electrical conductivity (EC) and Cd concentrations in Toyama soil solutions

○ : Unwashed, ● : Washed.

and 3b). Changes in EC and pH were attributed to the nitrification of urea, which increased Cd desorption from the soil[2]. Therefore, pH and EC are the primary factors controlling the release of Cd from soils.

Figures 4 and 5 show the changes in anion concentrations in soil solution from unwashed and washed soils during spinach growth. The behavior of NO_3^- resembled that of Cd in soil solution during the growth season in Fukuoka and Toyama soils. A strong correlation was observed between NO_3^- and Cd (Table 3; R^2 values of unwashed and washed soils: 0.76 and 0.629, respectively) in Fukuoka soil. The R^2 value between Cd and NO_3^- was also high (Table 4; R^2 values for unwashed and washed soils: 0.751 and 0.727, respectively) in Toyama soil. Therefore, the different pattern between Fukuoka and Toyama soils on the Cd concentration in soil solution during the growth season is attributable to the behavior of NO_3^-. NO_3^- correlated with pH (Table 3; R^2 values of unwashed and washed soils in Fukuoka: 0.403 and 0.464, respectively; Table 4, R^2 values of unwashed and washed soils in Toyama: 0.346 and 0.266, respectively). In addition, NO_3^- was strongly correlated with EC (Table 3; R^2 values of unwashed and washed soils in Fukuoka: 0.850 and 0.821, respectively; Table 4, R^2 values of unwashed and washed soils in Toyama: 0.839 and 0.703, respectively). The generation of NO_3^- (nitrification) may have affected the Cd concentration in the soil solution reflecting the decrease in pH and increase in EC. SO_4^{2-} was one of the main anions during the growth season in Fukuoka

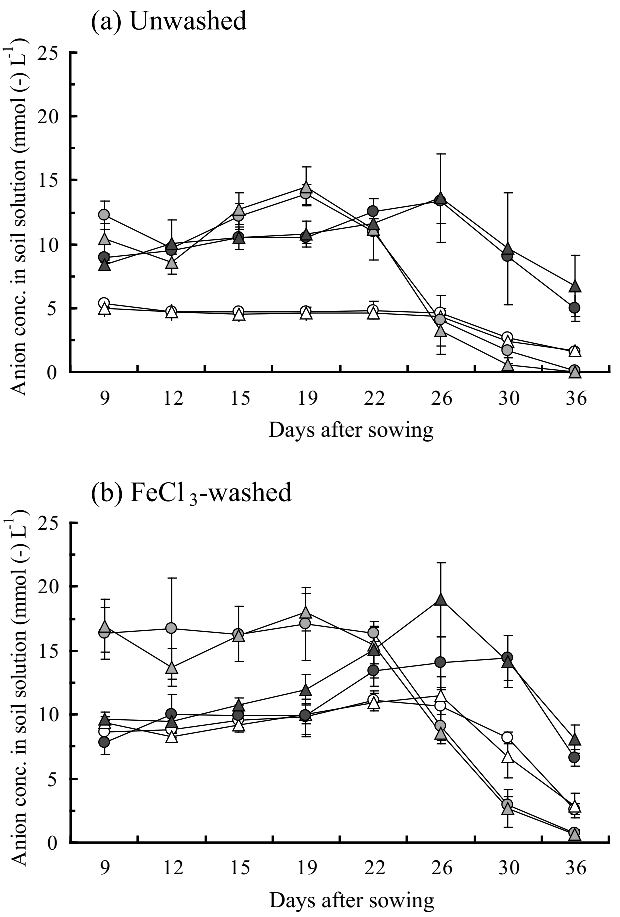

Fig. 4. Changes in anion concentrations in Fukuoka soil solutions from $FeCl_3$-washed plots during the pot experiments. Error bars indicate standard deviations (n = 3)

A, Active; BP, Banchu Palk.
○ : Chloride (A), △ : Choride (BP),
● (grey) : Nitrate (A), ▲ (grey) : Nitrate (BP),
● : Sulfate (A), ▲ :Sulfate (BP)

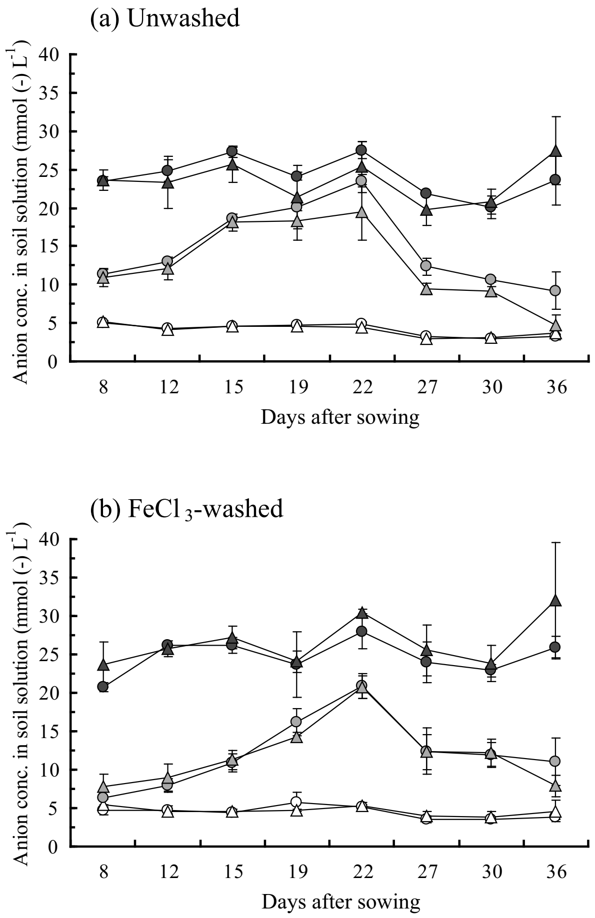

Fig. 5. Changes in anion concentrations in Toyama soil solutions from $FeCl_3$-washed plots during the pot experiments. Error bars indicate standard deviations (n = 3)

A, Active; BP, Banchu Palk.
○ : Chloride (A), △ :Choride (BP),
● (grey) : Nitrate (A), ▲ (grey) : Nitrate (BP),
● : Sulfate (A), ▲ :Sulfate (BP)

Table 3. Relationships (R^2 correlation) between electrical conductivity (EC), pH, anions, and cadmium (Cd) in Fukuoka soil solutions

		EC	Cl^-	NO_3^-	SO_4^{2-}	Cd
pH	Un-W	0.454	0.330	0.403	0.237	0.607
	W	0.621	0.386	0.464	0.051	0.677
EC	Un-W	–	0.861	0.850	0.275	0.896
	W	–	0.796	0.821	0.072	0.795
Cl^-	Un-W	–	–	0.640	0.444	0.779
	W	–	–	0.535	0.36	0.559
NO_3^-	Un-W	–	–	–	0.101	0.76
	W	–	–	–	0.001	0.629
SO_4^{2-}	Un-W	–	–	–	–	0.244
	W	–	–	–	–	0.053

Un-W: unwashed, W: $FeCl_3$-washed.

Table 4. Relationships (R^2 correlation) between electrical conductivity (EC), pH, anions, and cadmium (Cd) in Toyama soil solutions

		EC	Cl^-	NO_3^-	SO_4^{2-}	Cd
pH	Un-W	0.217	0.009	0.346	0.058	0.633
	W	0.074	0.091	0.266	0.090	0.532
EC	Un-W	–	0.598	0.839	0.314	0.618
	W	–	0.293	0.703	0.216	0.337
Cl^-	Un-W	–	–	0.355	0.306	0.130
	W	–	–	0.087	0.14	0.000
NO_3^-	Un-W	–	–	–	0.132	0.751
	W	–	–	–	0.097	0.727
SO_4^{2-}	Un-W	–	–	–	–	0.251
	W	–	–	–	–	0.189

Un-W: unwashed, W: $FeCl_3$-washed.

and Toyama soils (Figs. 4 and 5). The R^2 values between SO_4^{2-} and Cd in unwashed and washed soils were 0.244 and 0.053, respectively, in Fukuoka soil (Table 3), and 0.251 and 0.189, respectively, in Toyama soil (Table 4). Its behavior did not resemble that of Cd in soil solution (Figs. 4 and 5), thus, there were low correlation between SO_4^{2-} and Cd.

The anions affected Cd absorption by the crops. In other words, high concentrations of Cl^- in the soil stimulated Cd uptake and translocation by plants[15]. A positive correlation was observed between the total soluble Cd concentration and the Cl^- concentration in soil solution[6]. The increased solubility and availability of soil Cd can be attributed to the formation of $CdCl_2$ complexes[22,23]. In the Fukuoka soils (Fig. 4), a strong correlation was identified between Cl^- and Cd (Table 3; R^2 values of unwashed and washed soils: 0.779 and 0.559, respectively). In contrast, a weak correlation was observed between Cl^- and Cd in soil solution in the Toyama soil (Table 4; R^2 values of unwashed and washed soils: 0.130 and 0.000, respectively). Although the reason for the difference in R^2 values in Fukuoka and Toyama soil remains unclear, it might be attributable to the fluctuation range of Cl^- concentration during the growth season which was higher in Fukuoka soil compared to that in Toyama soil.

3. Comparison of the yield and Cd concentration between spinach leaves grown in $FeCl_3$-washed and unwashed soils

No significant difference was found in the yields of spinach cultivations between washed and unwashed soils (Fig. 6) and changes in exchangeable cations after soil washing had no effect on crop growth. However, the mean leaf Cd concentrations were approximately 60–70% lower in washed than unwashed soils (Fig. 7). The rate of decrease in Cd content in spinach was equal to that of the 0.1 M HCl-

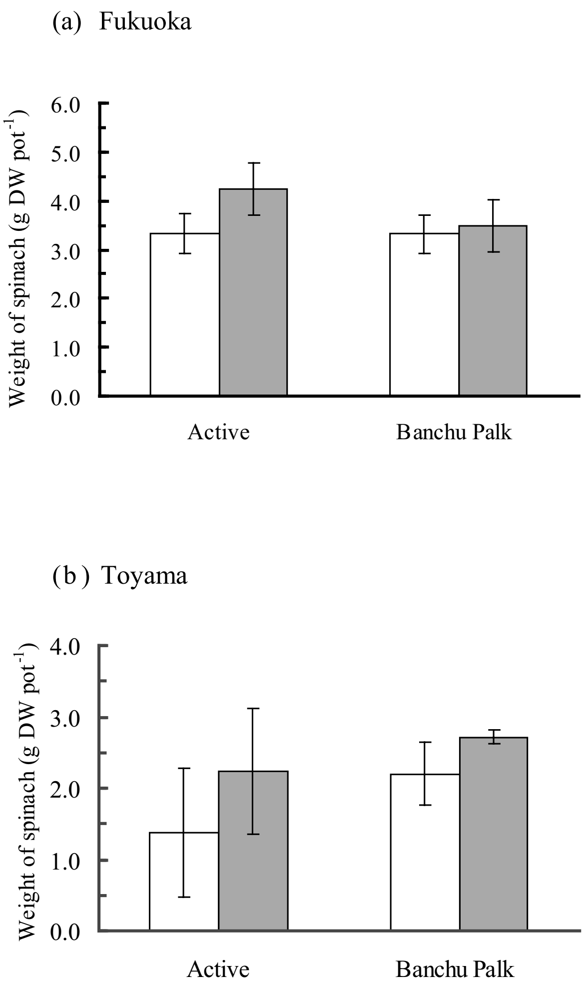

Fig. 6. Comparison of the dry weight (DW) between spinach from unwashed and $FeCl_3$-washed soils. Error bars indicate standard deviations (n = 3)
□ : Unwashed, ■ :Washed

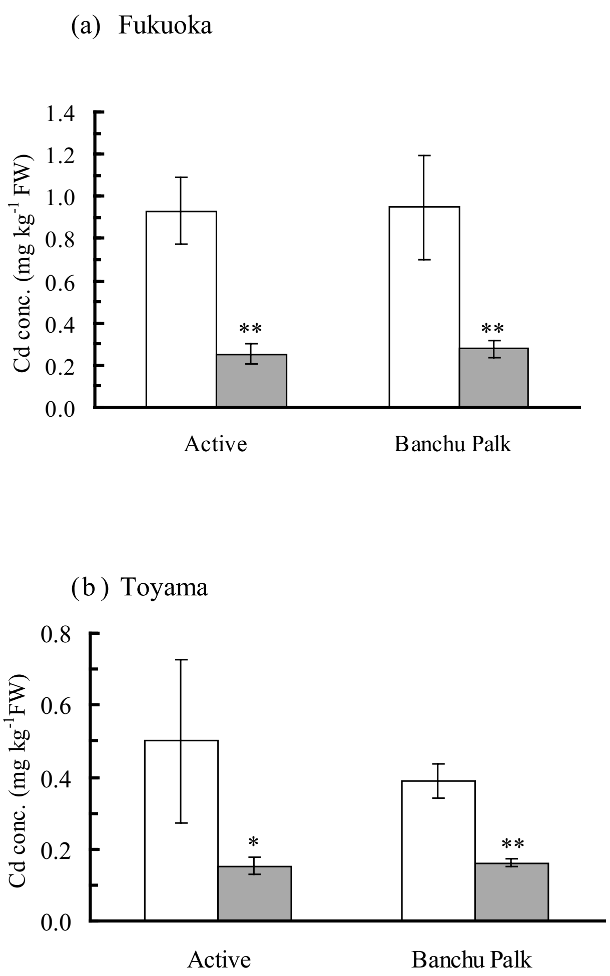

Fig. 7. Comparison of cadmium (Cd) concentrations between spinach from unwashed and $FeCl_3$-washed soils. Error bars indicate standard deviations (n = 3)
* and **: significant at the 0.05 and 0.01 probability levels, respectively.
□ : Unwashed, ■ :Washed

extractable Cd concentration in the soil, and Cl^- might not affect Cd absorption by spinach, which showed that soil washing with $FeCl_3$ could effectively reduce the soil Cd concentration and Cd absorption by spinach.

The Cd concentration in spinach in the Fukuoka washed plot was not less than the CODEX standard value (0.2 mg kg^{-1}) (Fig. 7a). The risk of Cd solubilization in upland field soil exceeds that in rice paddy field soils due to oxidative conditions in upland fields. Akahane et al.[2] reported that water-soluble Cd content in upland soils increased, pH decreased, and EC increased due to nitrification by nitrate fertilizers such as urea. Although the soil pH was adjusted to 6 using $CaCO_3$ before sowing, pH values after cultivation had almost decreased (Tables 1 and 2). In addition, the post-cultivation values for EC exceeded those before cultivation (Tables 1 and 2). It is important to use a delayed-release fertilizer such as manure to control the decline in pH and increase in EC due to nitrification. Fertilization systems must also be constructed considering the Cd absorption risk in upland crop plants. Soil washing may also possibly need to be combined with a countermeasure in some areas to clear the CODEX standard value in leafy vegetables such as spinach, which has a high Cd absorptive capacity.

Conclusions

This study was conducted to determine the effects of soil washing with $FeCl_3$ on the Cd uptake by spinach which has a high tendency to accumulate Cd. Soil washing with $FeCl_3$ greatly lowered the Cd concentration in soil and soil solution, and the Cd absorption by spinach decreased accordingly. The washing treatment had little effect on the growth of both spinach cultivars. Thus, we conclude that soil washing with $FeCl_3$ can reduce the risk of Cd absorption by leafy vegetables.

Acknowledgments

The authors gratefully acknowledge the useful suggestions provided throughout this work by T. Nishio, T. Arao, Y. Sakurai, and S. Ono of the National Institute for Agro-Environmental Sciences. We also thank Ms. M. Ochida, Ms. J. Hino, Ms. Sarina, Ms. M. Oda, and Mr. A. Suda for their assistance in the experiments.

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