Chemical remediation of cadmium-contaminated paddy soils by washing with ferric chloride: Cd extraction mechanism and on-site verification

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Abstract

Codex Alimentarius Commission (Codex) has adopted the maximum permissible concentration of cadmium (Cd) in polished rice and other relevant crops, which requires an alleviation of the Cd contamination in rice grain. Various chemicals were tested for their Cd extraction efficiency by using three paddy soils, selecting ferric chloride ($FeCl_3$) as a promising chemical for on-site soil washing. The comparison of $FeCl_3$ extraction ability to that of various iron, manganese, and zinc salts revealed the primary extraction mechanism of $FeCl_3$ to be proton release coupled with hydroxide generation (hydrolysis). This indicates that proton release from $FeCl_3$ is controlled by the chemical equilibrium of hydroxide formation, and minimizes the negative effect on soil properties and environment, which are different from hydrochloric acid (HCl). Washing with $FeCl_3$ led to the formation of Cd–chloride complexes, enhancing Cd extraction from the soils. We also developed in situ three-step washing method for Cd-contaminated paddy fields with $FeCl_3$. The method comprised 1) chemically washing the field soil with a $FeCl_3$ solution; 2) washing the treated soil with water to eliminate residual Cd and $FeCl_3$; and 3) on-site treatment of wastewater using a portable wastewater treatment system. Concentrations of Cd in the treated water were below Japan's environmental quality standard (0.01 mg/L). The on-site soil washing confirmed the effectiveness of $FeCl_3$ for decreasing Cd in soil and rice grains without negative effect on rice yield.

Key Words

Heavy metal, cadmium, remediation, soil washing, rice.

Introduction

Japanese agricultural soils, in particular, paddy soils in some regions, have been heavily polluted with cadmium (Cd), owing to fast industrialization during the 1960s. The Japanese government enacted the Agricultural Land Soil Pollution Prevention Law in 1970 which demarcated Cd-contaminated paddy fields which produced rice grains containing more than 1 mg/kg. Since the Law was in effect, the polluted paddy soils have been remedied mainly by unpolluted soil dressing. However, Codex has adopted the maximum permissible concentration of Cd in polished rice (0.4 mg/kg), which requires an alleviation of the Cd contamination in rice grain. In addition, the soil dressing has become increasing difficult to implement because of its high cost and difficulty in obtaining unpolluted soil. Thus, it is a matter of urgency to develop promising technologies to remediate the Cd polluted paddy soils. On-site soil washing could be one of the promising technologies, which is suitable for paddy fields which usually have an impervious layer that keeps the wash solution in the surface layer. For application of the soil-wash method to paddy fields, we have set up four points to guide the development of potential on-site remedial technologies for Cd-contaminated paddy soils; (1) selection of chemicals that have low environmental impact but high efficiency, (2) development of an on-site washing and wastewater-treatment system, (3) ensuring favorable post-washing soil fertility and plant growth and (4) maintenance of the washing effect (Makino *et al.* 2007).

As washing chemicals, strong metal chelatings, neutral salts and strong acids have been used (Davis, 2000). Especially, ethylenediaminetetraacetic acid (EDTA) could efficiently remove Cd from contaminated soils (Abumaizar and Smith 1999). EDTA, however, has the disadvantage of remaining in the environment for quite some time due to its low biodegradability (Tandy *et al.* 2004). Because EDTA has a high environmental burden, some researchers have used biodegradable chelating agent (Tandy *et al.* 2004). Though biodegradable chelating agents are favorable washing chemicals from the viewpoint of environmental impact, the costs of these chemicals are relatively high. Cost-effective and environmentally friendly chemicals are needed for soil washing. This paper aimed the selection of the promising extraction agents and developed the on-site soil washing for Cd-contaminated paddy fields.

Methods
Selection of washing chemicals
Three paddy soils were used for a Cd extraction test: Nagano soil (Fluvaquents), Toyama soil (Epiaquepts), and Hyogo soil (Fluvaquents). 10 g each of the three paddy soils polluted with Cd were shaken for 1hr with 15 ml of solutions containing 20 or 100 $mmol_c$/L chemicals such as acids, chelating materials, neutral salts, iron salts, manganese salts and zinc salts to extract Cd from soils. The Cd in the extracts was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Extraction with metal salts
Same extraction procedure, as mentioned above, was conducted using the three soils and 100 $mmol_c$/L of a variety of acids and metal salts, such as HCl, HNO_3, H_2SO_4, $FeCl_3$, $MnCl_2$, $ZnCl_2$, $Fe(NO_3)_3$, $Mn(NO_3)_2$, $Zn(NO_3)_2$, $Fe_2(SO_4)_3$, $MnSO_4$, and $ZnSO_4$. Various ions extracted using $FeCl_3$, $Fe(NO_3)_3$, and $Fe_2(SO_4)_3$ were determined by the following analytical methods with duplicate: ICP-OES for Na, K, Ca, and Mg, and distillation with MgO for NH_4+. An ion chromatograph (DX-320, Dionex Corp., USA) was used to measure anions (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}). Dissolved organic carbon (DOC) was analyzed using a total organic carbon analyzer (TOC-5000, Shimadzu Corp., Japan). Visual MINTEQ software was used to analyze the ionic, DOC, and pH data sets to estimate Cd speciation in the extracts (Gustafsson 2004).

On-site soil washing
An on-site testing plot (ca. 100 m^2) was prepared in a paddy field in Nagano Prefecture. The soil-washing procedure consisted of three steps: (1) chemical washing with $FeCl_3$ solution, (2) following water washing to eliminate the remaining chemicals, and (3) on-site treatment of the wastewater by a portable purification system with a chelating material. Soil samples were taken from the washed and unwashed plots. 0.1 mol/L HCl was used to extract soil Cd and the amounts of Cd extracted were determined by ICP-OES. Soil pH, electrical conductivity, total-C, total-N, available P, available N, and exchangeable cations were determined before and after soil washing. Rice plant was transplanted into the paddy field. Rice yields were measured after harvest. Part of the rice straw and some of the brown rice were ground, and digested with concentrated HNO_3 and then $HClO_4$. The Cd concentrations in the solutions were determined by ICP-OES.

Table 1. Soil properties (Makino *et al.* 2006).

Sampling site	Horizon	Depth cm	pH(H_2O)	pH(KCl)	[a]TC	[b]TN	[c]TCd	Clay	Silt	Sand	*Clay minerals	**Soil type
					g/kg		mg/kg		%			
Nagano	Ap	0–12	5.77	4.6	26.4	2.3	0.71	16.3	29.9	53.9	Kl, Ch, Mi	Fluvaquents
Hyogo	Ap	0–11	6.77	5.87	21.4	1.8	4.65	16.6	21.2	62.2	Kl, Ch, Mi	Fluvaquents
Toyama	Ap	0–10	4.96	3.87	15.6	1.4	1.21	15.3	17.6	67.1	Kl–Ch–Sm, Ch, Sm	Epiaquepts

Kl:kaolin minerals, Sm:smectite, Ch:chlorite, Mi:mica, Ch-Sm:chlorite-smectite intergrade.
**Classified by Soil Taxnomy (Soil Survey Staff 1998). [a]TC, [b]TN and [c]TCd indicate total carbon, total nitrogen and total Cd, respectively.

Results
The extraction efficiency of the neutral salt was relatively low compared with that of the strong acids. $FeCl_3$ extracted more than 90% of the total Cd extractable by the strong acids and EDTA (Figure 1)(Makino *et al.* 2006). Based on the results obtained, $FeCl_3$ was selected as an extracting agent in terms of its extraction efficiency and environmental friendliness. The Cd extraction capacity was compared with other metal salts to elucidate the mechanism of Cd extraction by $FeCl_3$. The proportion of total soil Cd extracted by the washing chemicals (i.e., the Cd extraction efficiency) increased in the following order: Mn salts $\leq$ Zn salts $<<$ ferric Fe salts in all the three soils, with efficiencies ranging from 4-41%, 8-44%, and 24-66%, respectively (Figure 2) (Makino *et al.* 2008). The amount of Cd extracted was negatively correlated with the extraction pH, suggesting that extraction pH plays an important role in determining the Cd extraction efficiency. When metal salts are added to soils, the dissociated metal cations that may form hydroxide precipitates with releasing protons according to the following equations (Hydrolysis):

$$M_mA_n = mM^{n+} + nA^{m-} \tag{1}$$
$$M^{n+} + nH_2O = M(OH)_n + nH^+ \tag{2}$$
$$K^{\circ}m = \frac{[M(OH)_n][H^+]^n}{[M^{n+}][H_2O]^n} \tag{3}$$

where M_mA_n denotes a metal salt, M a metal cation (Fe, Zn, or Mn) and A an anion (Cl^-, NO_3^-, or SO_4^{2-}). *m* and *n* represent the charge numbers of the anion and cation respectively. $K^{\circ}m$ denotes the equilibrium

constants (expressed in terms of activities) for metal M^{n+} in Eq. (2), corresponding to 2.88×10^{-4}, 3.31×10^{-13}, and 6.46×10^{-16} for Fe^{3+}, Zn^{2+}, and Mn^{2+}, respectively (Lindsay, 1979).

The precipitation of the metal hydroxide (hydrolysis of the metal ion) generates protons at a rate that depends on $K^o m$, and these protons may decrease the extraction pH (Eqs. 1-3). Figure 3 illustrates the theoretical relationships between pH and activity of metal ions in the metal hydrolysis reactions at the equilibrium with soil iron (calculated using Eq. 3 and the $K^o m$ values). The pH of ferric hydroxide is around 2 (Figure 3), which is much lower than the original soil-pH (H_2O) of the three soils. Thus, the Fe-hydrolysis is associated with a high decrease in soil pH compared to other two metals. This indicates that a driving force of the Cd extraction by $FeCl_3$ is proton release, which results in a sharp decrease in soil pH. Heavy metal solubilization was greatly enhanced by acidification, and at pH 1.3, reached more than 80% of the total Cd content of the soil (Dube and Galvez-Cloutier, 2005). Our results and these previous reports endorse the effectiveness of iron salts as washing chemicals to remove soil Cd. Determination of the chemical speciation of Cd using MINTEQ software indicated that Cd–chloride complexes were formed, and this would enhance Cd extraction from the soils (data not shown).
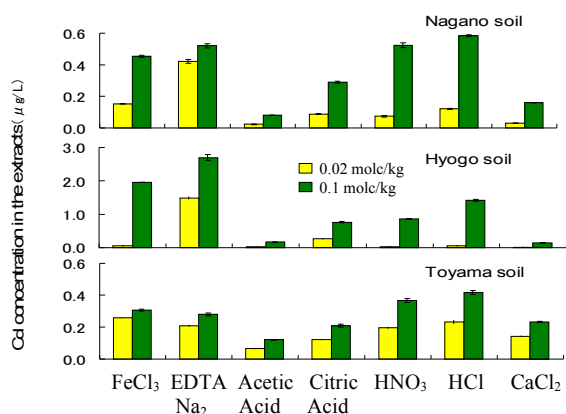

Figure 1. Efficiency of Cd extraction with various chemicals from the three soils.
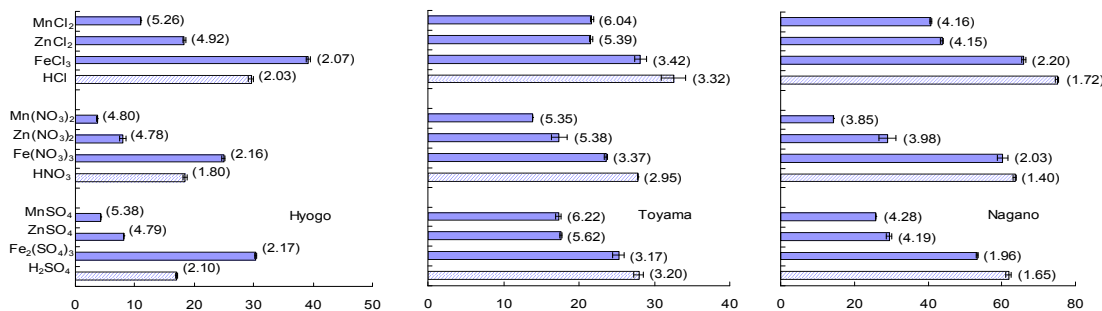

Figure 2. Comparison of cadmium extraction efficiency from the three soils by metal salts (gray bars) and strong acids (shaded bars). The extraction pH is shown in the parenthesis.
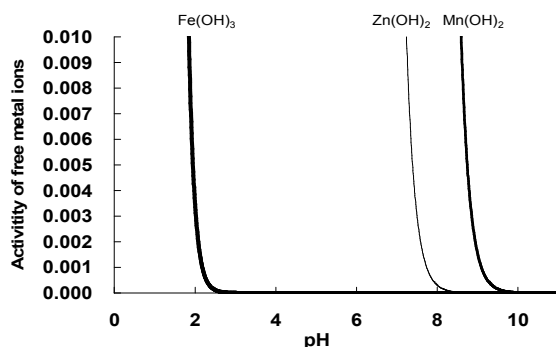

Figure 3. Diagram of pH and metal activity to precipitate metal hydroxides

During soil washing, the Cd concentration in the wastewater treated by the portable purification system was far below Japan's environmental quality standard (0.01 mg/L), proving that this technology was effective and promising for *in situ* treatment of wastewater. The Cl concentration was less than 500 mg/L after three times' washing by water. This concentration is the threshold value for healthy rice crops.

The Cd content extracted with 0.1MHCl in the washed soils was 55% of that in unwashed soils. The washing markedly decreased the Cd concentration (Figure 4). The pH(H_2O) and pH(KCl) of the soil were significantly decreased by on-site washing treatment. The soil EC increased with the treatment; however, it did not reach the critical level at which rice growth starts to retard. Exchangeable cations were decreased by soil washing. The Mg and K deficit was corrected by application of fertilizers to the washed soil. Total carbon and total nitrogen content were scarcely changed by washing.

Although changes in some relevant soil properties were observed, the changes can be easily corrected and does not affect relevant soil fertility. Soil washing considerably decreased the Cd content in the rice straw and brown rice from 0.91 and 0.31 mg/kg, respectively in the unwashed soil, to 0.18 and 0.053 mg/kg in the washed soil (Figure 5).
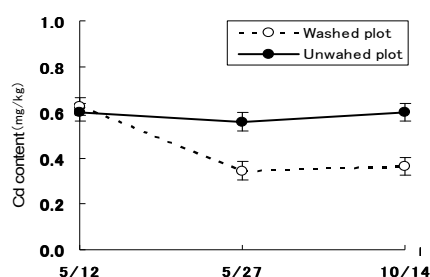
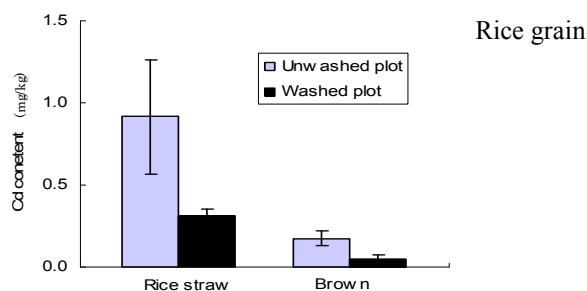**Figure 4. Changes of Cd contents in soils with washing treatment extracted with 0.1M HCl.**

Figure 5. Effects of the washing treatment on the Cd contents in rice grain.

Conclusion

We selected ferric iron chloride for soil washing and revealed primary extraction mechanism of $FeCl_3$ is proton release coupled with hydroxide generation. We also developed an on-site soil washing technology for Cd-contaminated paddy fields. The washing had no negative affect on rice growth, and reduced the average Cd concentration in soil and rice grains.

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