Advanced Physico-chemical Method to Restore Agricultural Soils Contaminated with Cd and Radioactive Cesium

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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 to select the promise extraction agents and developed the on-site soil washing for Cd-contaminated paddy fields.

On the other hand, the leakage of radionuclides due to the accident at the Tokyo Electric Power Fukushima Daiichi nuclear power plant contaminated a vast expanse of farmland with radioactive cesium. The decontamination of these contaminated areas is a major challenge for society. Since the accident, therefore, radioactive cesium has accumulated in the uppermost soil layer (about 0–2 cm) of untilled fields, and stripping off the topsoil has been considered to be an effective decontamination method. Surface soil layer stripping was carried out after the 1986 Chernobyl nuclear accident (Vovk et al., 2004), and the Decontamination Guidelines by Japan’s Ministry of the Environment likewise includes this as one of the main decontamination methods for untilled farmland (Ministry of the Environment, 2013). But it is difficult to use surface layer stripping for cultivated farmland, and in Ministry of the Environment decontamination projects, decontamination by inversion tillage or deep tillage is eligible for assistance when decontaminating cultivated farmland; however, inversion tillage and deep tillage are hard to use in cases where the plow layer is not thick enough or there is gravel layer directly below the plow layer. New decontamination measures that can be used on cultivated farmland are needed.

2. Theoretical Basis for Soil Washing Technologies

2.1 Adsorption and chemical forms of pollutants in soils

The various chemical forms of heavy metals in soils determine their response to countermeasures. Because there are various mechanisms of sorption of ions, it is important to understand the chemical form of heavy metals in soils before remediation is attempted. Successive extractions by various extraction solvents are useful in clarifying the chemical forms of heavy metals in soils and the mechanisms of sorption. The relationship between extraction methods and chemical forms of heavy metals is summarized in Table 1 (Makino, et al. 2006). This difference among heavy metals can be explained by the interaction between soil and heavy metals. In usual soil, the ratio of exchangeable Cd to total content is higher than that of Zn and Cu. Hydroxyl groups on the surface of allophane, goethite, and ferrihydrite and on the edge of phyllosilicates in soils lose hydration water and form an inner-sphere complex with heavy metals through coordination bonding. As the selectivity sequence for the adsorption or coprecipitation of heavy metal cations on various hydrous metal oxides shows, the selectivity of Cd on hydrous metal oxides is lower than that of Zn and Cu, explaining why the ratio of exchangeable form to total content increased. In some cases, the ratio of exchangeable Cd decreases in unpolluted soil, sources of heavy metals and the polluted period affect the chemical form of Cd. On the other hand, Cu has a high capacity to complex with organic matter. The stability constant of Cu (at pH 5) with humic acid is the highest among some heavy metals. Thus, the ratio of the organic bonded form is higher in Cu than in other heavy metals (Makino, et al. 2008).

On the other hand, because radioactive cesium is strongly adsorbed by the frayed edge sites of soil colloids and by six-member silicate rings, radioactive cesium that has fallen on farmland stays in the superficial soil layer and very little moves to lower layers even after the rainy season. The primary adsorption mechanism of organic pollutants is hydrophobic interaction on organic colloids. Coordination exchange, protonation, hydrogen bond, cation bridge and water bridge also work on the adsorption of organic pollutants.
Table 1  Chemical forms and sorption mechanisms of heavy metals in soils based on successive extractions.

<table>
<thead>
<tr>
<th>Chemical form</th>
<th>Treatment</th>
<th>Sorption mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>Extraction by neutral salt solution</td>
<td>Electrostatic adsorption on charged sites caused by isomorphic substitution in phyllosilicates, etc. (Outer sphere complex)</td>
</tr>
<tr>
<td>Inorganically bound</td>
<td>Extraction by dilute acid, acetic acid, etc.</td>
<td>Adsorption on the edge face of phyllosilicates or surface hydroxyl groups through ligand exchange, covalent bonding, hydrogen bonding (Inner sphere complex). Includes some sorption through polymer formation by dehydration- condensation reaction and surface precipitation</td>
</tr>
<tr>
<td>Organically bound</td>
<td>Extraction by sodium pyrophosphate solution, or decomposition by hydrogen peroxide followed by acetic acid extraction</td>
<td>Binding with soil humus through complexation</td>
</tr>
<tr>
<td>Oxide-occluded</td>
<td>Extraction by hydroxylamine chloride for manganese oxides. Extraction by ammonium oxalate with ascorbic acid for iron oxides</td>
<td>Occluded in iron and manganese oxides, which are produced by coprecipitation during oxide formation, and by lattice diffusion and isomorphic substitution within the mineral lattice.</td>
</tr>
<tr>
<td>Residual</td>
<td>Decomposition by strong acid (nitric acid, hydrochloric acid, perchloric acid, sulfuric acid and hydrofluoric acid)</td>
<td>Present in mineral lattice</td>
</tr>
</tbody>
</table>

2.2. Type of soil washing

Processes to remove hazardous chemicals by soil washing are divided mainly into two types: particle size separation and contaminant extraction. The former method involves reducing volume by separating soil particles by size while washing contaminated soil with water, and dividing soil into clean and contaminated soil (Anderson, 1993). Generally, the smaller the size of soil particles, the higher the relative concentration of contaminants. This makes it possible to remove contamination by separating out fine particles. Devices used for this include screw separators and wet cyclones (Anderson, 1993). The latter type is a remedial technology that adds cleaning materials to contaminated soil by mixing them in liquid form, extracts the hazardous chemicals from the soil in the liquid phase, and then processes the effluent with a purification system.

2.3 Separation theory for size-fractionation of soil particle

Traditional fractionation methods for natural colloids include sieve, settling, centrifugation, and membrane filtration. The separation theory of settling method is based on Stokes’ law as mentioned below.

\[
d = \sqrt{\frac{18\eta h}{g(\rho_p - \rho_l)}}
\]

where \(d\) is particle size (m), \(\rho_p\) is particle density (kg m\(^{-3}\)), \(\rho_l\) is water density (kg m\(^{-3}\)), and \(\eta\) is the coefficient of water viscosity (Pa s).

Although natural settling method (gravity sedimentation) is available for size fractionation of soil micro particle whose diameter is micro to submicron, Continuous-flow ultracentrifugation (CFUC) has been used for the separation of viral particles from large volumes of culture fluid (Round et al., 1981). CFUC has some advantages for the size-fractionation in terms of speed and efficiency. As mentioned by Makino et al. (2011), CFUC (Hitachi Co., CR-22G, Japan) which we have used to separate the samples into \(\phi < 1, 0.6, \) and 0.2 \(\mu\)m fractions (Stokes radius) in lab-scale experiment (Makino et al., 2011). The clay and soil suspensions were continuously pumped into a rotating rotor in the ultracentrifuge (Fig. 1 and 2). The pumping rate was set at 250 mL min\(^{-1}\) based on preliminary experiments, and the rotor speed was determined on the basis of separation theory. The pumped suspension flows along the core and forms flow channel in the rotor as shown by the arrows in Fig. 2. During the flow in the flow channel, size fractionation occurs on the basis of the rotor speed and pumping rate according to Stokes’ law, and some of relatively larger SMP which derailed from the flow channel precipitate on the inside wall of the rotor body. The width of the flow channel is the difference of \(r_{\text{min}}\) and \(r_{\text{max}}\), which are the radius of the core surface in the rotor and the maximum radius at which particles derailed from the flow channel, respectively.
Spragg and Steensgaard (1992) mentioned the efficiency of all centrifuge rotors is traditionally expressed in terms of $k$ factors. Using water as centrifuge medium the rotation time in hours ($t_1$) required to pellet a particle is given by Eq. 1:

$$t_1 = \frac{k}{S} \quad (1)$$

where $S$ is the sedimentation constant of the particle in Svedberg units ($10^{-13}$ sec). From the definition of the sedimentation constant it can be seen that:

$$S \omega^2 t_1 = (\ln r_{max} - \ln r_{min}) \quad (2)$$

$r_{max}$ is the maximum radius at which particles settle in the rotor (6.67 cm in Fig. 2), $r_{min}$ is the radius of the core surface in the rotor (5.5 cm in Fig. 2), and $\omega$ is angular velocity (radian/sec) described by:

$$\omega = \frac{2 \pi N}{60} \quad (3)$$

where $N$ is revolutions of rotor per minute (rpm).

Substituting Eq. 1 and 3 into Eq. 2, we obtain the following equation for the $k$ factor:

$$k = \frac{\ln r_{max} - \ln r_{min}}{4\pi^2 N^2} \times 10^{13} \quad (4)$$

On the other hand, Rickwood (1984) mentioned sedimentation constant $S$ is expressed by:

$$S = \frac{d^2(\rho_s - \rho_l)}{18 \times \eta} \times 10^{13} \quad (5)$$

where $d$ is particle size (cm), $\rho_s$ is particle density (2.6 g cm$^{-3}$), $\rho_l$ is water density (g cm$^{-3}$), and $\eta$ is the coefficient of water viscosity (poise).

The flow time of suspension in the flow channel $t_2$ (h) is described by:

$$t_2 = \frac{v}{Q} \quad (6)$$

where $v$ is the volume of the flow channel in the rotor (cm$^3$) and $Q$ is the flow rate of the suspension (cm$^3$ s$^{-1}$).

At $t_1 = t_2$, Eq. 1 and Eq. 6 can be combined to provide Eq. 7. In this case, particles with sedimentation constants larger than $S$ derail from the flow channel and precipitate on the inside wall of the rotor body.

$$\frac{k}{S} = \frac{v}{Q} \quad (7)$$

Substituting Eq. 5 into Eq. 7 and rewriting it as a commutative expression, we obtain

$$d = \sqrt[6]{\frac{18Qk \eta}{v(\rho_s - \rho_l)} \times 10^{13}} \quad (8)$$

Thus, if $Q$ is constant, separated particle size $d$ is determined by $Q$ and $N$ based on Eq. 4 and Eq. 8.
3. Soil washing for paddy fields contaminated with Cd

3.1 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 L⁻¹ 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).

The extraction efficiency of the neutral salt was relatively low compared with that of the strong acids. FeCl₃ extracted more than 90% of the total Cd extractable by the strong acids and EDTA (Fig. 3) (Makino et al., 2006). Based on the results obtained, FeCl₃ was selected as an extracting agent in terms of its extraction efficiency and environmental friendliness.

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

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Depth cm</th>
<th>pH(H₂O)</th>
<th>pH(KCl)</th>
<th>*TCg/kg</th>
<th>*TNmg/kg</th>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand %</th>
<th>*Clay minerals</th>
<th>**Soil type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagano Ap</td>
<td>0-12</td>
<td>5.77</td>
<td>4.6</td>
<td>26.4</td>
<td>2.3</td>
<td>0.71</td>
<td>16.3</td>
<td>29.9</td>
<td>53.9</td>
<td>Fluvaquents</td>
</tr>
<tr>
<td>Hyogo Ap</td>
<td>0-11</td>
<td>6.77</td>
<td>5.87</td>
<td>21.4</td>
<td>1.8</td>
<td>4.65</td>
<td>16.6</td>
<td>21.2</td>
<td>62.2</td>
<td>Fluvaquents</td>
</tr>
<tr>
<td>Toyama Ap</td>
<td>0-10</td>
<td>4.96</td>
<td>3.87</td>
<td>15.6</td>
<td>1.4</td>
<td>1.21</td>
<td>15.3</td>
<td>17.6</td>
<td>67.1</td>
<td>Epiaquepts</td>
</tr>
</tbody>
</table>

*KL: kaolin minerals, Sm: smectite, Ch: chlorite, Mi: mica, Ch-Sm: chlorite-smectite intergrade.
**Classified by Soil Taxonomy (Soil Survey Staff, 1998). *TC, *TN and *TCd indicate total carbon, total nitrogen and total Cd, respectively.

![Fig. 3. Efficiency of Cd extraction with various chemicals from the three soils.](image)

3.2 Extraction with metal salts

Same extraction procedure, as mentioned above, was conducted using the three soils and 100 mmol L⁻¹ of a variety of acids and metal salts, such as HCl, HNO₃, H₂SO₄, FeCl₃, MnCl₂, ZnCl₂, Fe(NO₃)₃, Mn(NO₃)₂, Zn(NO₃)₂, Fe₂(SO₄)₃, MnSO₄, and ZnSO₄. Various ions extracted using FeCl₃, Fe(NO₃)₃, and Fe₂(SO₄)₃ were determined by the following analytical methods with duplicate: ICP-OES for Na, K, Ca, and Mg, and distillation with MgO for NH₄⁺. An ion chromatograph (DX-320, Dionex Corp., USA) was used to measure anions (Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻). 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).

The Cd extraction capacity was compared with other metal salts to elucidate the mechanism of Cd extraction by FeCl₃. The proportion of total soil Cd extracted by the washing chemicals (i.e., the Cd extraction efficiency) increased in the following order: Mn salts ≤ Zn salts << ferric Fe salts in all the three soils, with efficiencies ranging from 4-41%, 8-44%, and 24-66%, respectively (Fig. 4) (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):
\[ \text{MmAn} = m\text{M}^{n+} + n\text{A}^{-} \quad (1) \]

\[ \text{M}^{n+} + n\text{H}_2\text{O} = \text{M(OH)}_n + n\text{H}^+ \quad (2) \]

\[ K_m^a = \frac{[\text{M(OH)}_n][\text{H}^+]}{[\text{M}^{n+}][\text{H}_2\text{O}]} \quad (3) \]

where \( \text{MmAn} \) denotes a metal salt, \( \text{M} \) a metal cation (Fe, Zn, or Mn) and \( \text{A} \) an anion (Cl\(^-\), NO\(_3\)-, or SO\(_4\)^{2-}\)). \( m \) and \( n \) represent the charge numbers of the anion and cation respectively. \( K_m^a \) denotes the equilibrium constants (expressed in terms of activities) for metal \( \text{M}^{n+} \) in Eq. (2), corresponding to \( 2.88 \times 10^{-4}, 3.31 \times 10^{-13} \), and \( 6.46 \times 10^{-16} \) 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 \( K_m^a \), and these protons may decrease the extraction pH (Eqs. 1-3). Figure 5 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 \( K_m^a \) values). The pH of ferric hydroxide is around 2 (Fig. 5), which is much lower than the original soil-pH (H\(_2\)O) 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).

![Fig. 4. 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.](image)

![Fig. 5. Diagram of pH and metal activity to precipitate metal hydroxides](image)
3.3 On-site soil washing at Cd-contaminated paddy field

An on-site testing plot (ca. 100 m²) was prepared in paddy fields in Japan. The soil-washing procedure consisted of three steps: (1) chemical washing with FeCl₃ 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⁻¹ 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 HNO₃ and then HClO₄. The Cd concentrations in the solutions were determined by ICP-OES.

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⁻¹), proving that this technology was effective and promising for in situ treatment of wastewater. The Cl concentration was less than 500 mg L⁻¹ after three times' washing by water. This concentration is the threshold value for healthy rice crops.

The Cd content extracted with 0.1M HCl in the washed soils was 30-40% of that in unwashed soils (Cd reduction rate of 60–70%). The washing markedly decreased the Cd concentration. The pH(H₂O) 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 whose reduction rate were nearly reached around 70%, confirming availability of the soil washing method.

4. Soil washing for contaminated with radioactive Cs (Cs-137)

As mentioned at section 2.1, Cs has a quite high adsorption activity to soil particles through the frayed edge sites of soil colloids and by six-member silicate rings. It is difficult to apply the soil washing based on contaminant extraction for Cs contamination without fatal damage to soil colloids. In this section, we refer soil washing based on particle size separation.

4.1 Particle size separation at a factory scale

Figure 6 shows an example of soil cleaning system that uses particle size separation (Anderson et al., 1999; Yamaguchi et al., 2012). The treatment process is comprised of the following stages. (1) For rough separation, soil particles are disaggregated in a trommel to separate soil particles from coarse particles. Coarse particles several mm or larger in diameter are cleaned with a high-pressure spray and sent to the ejection chute. (2) Soil particles smaller than several mm enter the first-stage screw separator, where the particles are classified into sand and fine particles smaller than sand based on Stoke’s Law. In this stage, the fine particles overflow and collect in the sump pit; the sand is then sent to the attrition mill, which rubs the sand particles together to remove fine particles adhering to the sand. Fine particles thus removed are merged with the fine particles from (2). (3) Fine particles are moved to the second screw separator, where particles are fractionated at a size of 0.25 mm; particles 0.25 mm and larger are recovered as clean soil, and the fraction under 0.25 mm is sent to the wet cyclone. (4) The wet cyclone is a machine that uses centrifugal force to separate by precipitation the fine particles dispersed in the suspension, and sorts them by particle size. Particles are fractionated at a size of 75 µm and then dewatered. (5) The hydraulic separator fractionates fine particles between 75 to 45 µm. The hydraulic separator separates particles based on Stoke’s Law and hindered settling. The fine particles gathered by the hydraulic separator are merged with the fine particles from the wet cyclone. (6) The ultimately obtained fine particles under 45 µm, which include Cs in high concentration, are coagulated with polymeric coagulant and recovered. Targeted particle sizes change depending on the process.
4.2 Practical soil washing for paddy fields contaminated with radioactive Cs by using natural settling

Much of Japan’s farmland is rice paddies, which can retain water in the surface layer. This makes it possible to inundate paddies, directly agitate their soil in place, and then drain off the fine soil particles, which have relatively high concentrations of radioactive cesium. Okushima et al. (2012) hypothesized that it would be possible to contribute to efficient decontamination of rice paddies by flooding radioactivity-contaminated untilled paddies, agitating the soil surface layer to suspend the fine particles in the water, pumping to remove the turbid water (shallow puddling and drainage), and selectively discharge the fine particles with high concentrations of radioactive cesium. They verified this in a container experiment. The container was filled with a 5-cm thick layer of radioactive cesium contaminated soil, water was added to a depth of 10 cm from the soil surface, the soil was agitated, and turbid water was drained. As a result, radioactive cesium (Cs-134 + Cs-137) concentrations in the soil decreased 39% from 25,900 Bq kg\(^{-1}\) before the experiment to 15,700 Bq kg\(^{-1}\) after.

Mizoguchi (2013) suggests a method that combines soil agitation using water with drainage and inversion tillage. This entails digging holes in parts of a field, and then, after puddling, flowing the muddy water into the holes using a device similar to the oil fence described above. It is a distinctive approach that cleans paddy soil and disposes of drained-away soil in situ.

4.3 Development of stirring cleaning method to remediate Cs-contaminated paddy fields

Paddy soils in general readily disperse under alkaline conditions as primary mineral is 1:1 and 2:1 types in the soil. We added sodium hydroxide as a soil dispersant after flooding and agitated the soil (Makino et al., 2013; Ministry of the Environment, 2014). Sodium hydroxide elevates pH and heightens the electrical repulsion of fine soil particles to one another, thereby highly dispersing fine soil particles.

Following is the process of stirring cleaning decontamination method that we carried out in a Fukushima Prefecture test paddy with gray lowland soil (Fig. 7).

1. A test plot of approximately 100 m\(^2\) was created in a paddy. It was plowed to a depth of about 7 cm using a tractor equipped with a laser-leveling sensor.
(2) The plot was flooded to a depth of 25 cm above the plow pan, sodium hydroxide pellets were added, the soil was agitated with cage wheels, and pH was adjusted to between 8 and 9.

(3) As soon as agitation finished, we started draining the soil suspension on the paddy surface with a pump, and collected the suspension in a coagulating sedimentation tank.

(4) Polyaluminum chloride and polymeric coagulant were added to the tank. The tank was stirred to coagulate and settle the suspended solids (SS), which consisted mainly of fine soil particles.

(5) The sediment of the coagulated solids was stored for a short time in the tank and other containers, then a filter press was used to separate the solids from the liquid, and the solids were recovered as sludge.

(6) After the paddy was drained, the plot was reflooded, and the agitation-drainage process was repeated three more times for a total of four times.

(7) After completing the agitation-drainage treatment, ferric chloride solution was added to the paddy, and it was stirred to return the soil to a pH of about 6.

Sampling and analysis were conducted as follows. (1) Aqueous suspensions were obtained from the drainage pump and used as samples for measuring the amount of SS and Cs-137 concentration. (2) Before and after decontamination, a soil corer sampler was used to take soil cores to a depth of 30 cm at five sites in the field. Soil cores were cut into sections (soil surface to 2 cm, 2–5 cm, 5–10 cm, 10–15 cm, and below 15 cm) to produce soil samples by depth. (3) Before and after decontamination, the air dose rate was measured with a scintillation survey meter, and radioactive cesium in soil and SS were measured with a NaI scintillation detector and a germanium detector, respectively.

The results are summarized below.

The air dose rate 1 m from ground level in the test field declined from 1.77 µSv h\(^{-1}\) before decontamination to 1.24 µSv h\(^{-1}\) after, for a reduction of 30.1%. The concentration of Cs-137 in the soil (total for 0–15 cm depth) decreased from 3.06 to 1.17 kBq kg\(^{-1}\), for a reduction of 61.7%. The amount of Cs-137 decrease calculated for the soil down to a depth of 30 cm, where radioactivity from Cs was not detected, was 31.3 MBq for the entire test plot (about 100 m\(^2\)). Four agitation-drainage treatment cycles removed 3.05 t of SS from the test plot. If volume-weight is set to a value of 1, this amount corresponds to a soil thickness of about 3 cm. The amount of Cs-137 removed from the test plot was 34.9 MBq when calculated from the amount of SS removed and the Cs-137 radiation concentration of the SS. Because this is about equal to the Cs-137 reduction amount in (2), the consistency of the Cs-137 balance for the plot was confirmed. (4) Radioactive cesium concentrations of the supernatant drained from coagulated clay and of the water from dewatering the coagulated clay in the filter press were below the detection limit (less than 1 Bq L\(^{-1}\)). The Maihime rice variety was cultivated in the paddy after stirring cleaning decontamination. Although the brown rice yield was 15% less than when the rice is cultivated without stirring cleaning decontamination (10% less than the targeted yield of 6 t ha\(^{-1}\)), yield recovery was possible with the use of fertilizer and other inputs. Additionally, radioactive cesium concentration in brown rice was reduced 60% to 17 Bq kg\(^{-1}\).

This method can also be applied to plowed rice paddies by adjusting the agitation depth.
Fig. 7. Practical process of soil cleaning system for paddy fields contaminated with radioactive Cs

5 Conclusions

We selected ferric iron chloride for soil washing on Cd contaminated paddy soils. We also revealed primary extraction mechanism of FeCl₃ 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.

As for radioactive Cs contamination in paddy fields, we have developed a new, stirring cleaning method to remediate Cs-contaminated paddy fields. The removal rate of Cs-137 from soil was 61.7% and can extensively decrease the amount of removed soil compared to the method of removal of contaminated surface soil. Cs-137 concentration in brown rice cultivated in the decontaminated paddy field was reduced by 60%.

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6. References


Dube JS, Galvez-Cloutier R. 2005: Applications of data on the mobility of heavy metals in contaminated soil to the definition of site-specific remediation criteria: Journal of Environmental Engineering and Science 4: 399-411.