Management of Heavy Metal Contamination in Japan

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Abstract

Rapid industrialization in the 1960s resulted in critical soil pollution by heavy metals such as cadmium (Cd) in Japan. Recently, the Codex Alimentarius Commission proposed a maximum permissible concentration of Cd and arsenic (As) in polished rice. Appropriate technologies to minimize the Cd/As contamination are discussed and proposed. These include (1) water management to decrease the bioavailability of soil Cd to rice plants, (2) dressing and/or replacement of polluted soil with non-polluted soil, (3) low-Cd-accumulating cultivars mutated by ion-beam radiation, (4) phytoremediation of polluted soil by rice and other promising crops, and (5) chemical remediation of Cd-polluted soil by soil-washing with chemicals such as iron salts. This paper also discusses promising methods to simultaneously decrease concentrations of As and Cd in rice grains.

Keywords: arsenic, cadmium, paddy soil, rice

1. Introduction

Japanese agricultural soils in some regions have been polluted with cadmium (Cd) and various other heavy metals, owing to rapid industrialization during the 1960s. The Japanese government urgently enacted the Agricultural Land Soil Pollution Prevention Law in 1970 to cope with the heavy metal pollution, of which Cd, arsenic (As), and copper (Cu) were targeted as hazardous substances for regulation. Cd, in particular, has been recognized as one of the most detrimental elements in Japan because of the so-called itai-itai disease caused by Cd poisoning. In some regions of Japan, flooded cultivation for 3 weeks before and after ear emergence has been recommended to decrease cadmium (Cd) concentrations in rice grains to values below those permitted (0.4 mg kg⁻¹).

In 2014, the Codex Alimentarius Commission proposed a maximum permitted concentration for inorganic As in polished rice of 0.2 mg kg⁻¹. However, in contrast to Cd uptake, As uptake by rice plants is markedly increased by flooded cultivation. Therefore, there is a tradeoff between As and Cd uptake by rice depending on the type of water management. Promising practical techniques to simultaneously diminish As and Cd in rice grains are urgently needed.

This article will provide an overview of state of the art technologies to minimize Cd and As contamination in soils and rice plants, which include: (1) breeding low adsorptive cultivars, (2) phytoremediation of polluted soil by rice plants, (3) chemical remediation of Cd-polluted soil
by soil-washing, and (4) promising methods to simultaneously decrease concentrations of As and Cd in rice grains.

Most of these research studies have been conducted by the National Institute for Agro-Environmental Sciences (NIAES) and collaborative research groups.

2. Countermeasures to minimize Cd Contamination in Rice Plants in Japan

1) Soil Dressing

Soil dressing is one of the best-known methods used for heavily contaminated sites (Vangronsveld and Cunningham, 1998). The Agricultural Land Soil Pollution Prevention Law in Japan has adopted soil dressing as a primary countermeasure for Cd contamination in agricultural soils, because it has a low risk of failure, a predictable time frame, and leaves the site in relatively pristine condition. Several variations of soil dressings are possible (Yamada, 2007), such as (1) placing unpolluted soil on top of polluted soil, (2) removing the polluted soil and refilling it with unpolluted soil, and (3) turning the soil layers upside down (exchanging the polluted topsoil with unpolluted subsoil). According to several follow-up surveys in Japan, soil dressing is a very effective and reliable practice to decrease Cd content in rice grains, when the newly dressed unpolluted soil layer is at least 20–30-cm thick. However, this practice is costly and becoming increasing difficult to implement because of the scarcity of suitable unpolluted soils.

2) Water Management

Water management is a popular and cost-effective cultural practice to minimize rice Cd contamination in Japan. Cadmium absorption by rice has been decreased drastically by continuous submergence of paddy fields after heading-time. It is likely that the considerable decrease in Cd absorption by rice under submerged conditions is because of a decrease in the Cd solubility, due to the formation of carbonates (Khaokaew et al., 2011) and/or CdS (Iimura and Ito, 1978; de Livera et al., 2011) as shown in Eqs. 1 and 2 (Lindsay, 1979). The former, Cd carbonate, primarily forms under alkaline conditions (Khaokaew et al., 2011), whereas the latter, CdS, may be the dominant form under slightly acidic conditions. When paddy fields are flooded, the paddy soil is rapidly reduced, and consequently, its redox potential (Eh) is shifted toward a reduced state (a sharp decrease in Eh), where sulfate ions get reduced to sulfide ions. The produced sulfide ions react with Cd to precipitate out of the soil solution as cadmium sulfide. The precipitation of cadmium sulfide, in turn, lowers the Cd concentration in the soil solution, resulting in a lowering of the amount of bioavailable Cd for rice plants. Flooding from tilling to head formation in the rice growth stage is the most effective period to decrease the Cd content in rice grains.

\[
\text{CdCO}_3 \text{ (Octavite)} + 2\text{H}^+ = \text{Cd}^{2+} + \text{CO}_2 \text{ (g)} + \text{H}_2\text{O} \quad \log K = 6.16 (1)
\]

\[
\text{CdS} \text{ (Greennokite)} = \text{Cd}^{2+} + \text{S}^{2-} \quad \log K = -27.07 (2)
\]
3) The Mutagenic Approach to decreasing Cd Content in Rice

Breeding low-Cd-accumulating cultivars is the most cost-effective and environmentally friendly method to decrease the risk of contamination from Cd in food (Grant et al., 2008). In this section, we introduce the first study of a practical rice cultivar with low-Cd traits developed using the mutagenesis approach (Ishikawa et al., 2012).

Isolation of low-Cd-accumulating rice mutants

Energetic heavy-ion beams have recently been used to generate novel mutants in higher plants because they induce mutations with high frequency at relatively low doses (i.e., at a dose where virtually all plants survive), and they induce a broad spectrum of phenotypes without affecting other plant characteristics (Tanaka et al., 2010). Using this technique, we irradiated seeds of the most popular Japanese temperate japonica rice cultivar, Koshihikari, with accelerated carbon ions. The resultant 2,592 M2 plants were grown in pots filled with Cd-polluted soil and the Cd concentration in each plant was analyzed. Three rice mutants (lcd-kmt1, lcd-kmt2, and lcd-kmt3) were identified in the first screening. The grain Cd concentration in wild-type (WT) Koshihikari averaged 1.73 mg kg⁻¹, whereas these mutants showed values <0.05 mg kg⁻¹. When the seedlings of the WT and the three mutants were exposed to Cd in hydroponics, the Cd and manganese (Mn) concentrations in the roots and shoots were significantly lower in the mutants than in the WT. This result suggests that the lcd-kmt mutants exhibited a decreased Cd uptake in their roots, and that Cd might be transported via the Mn pathway into the roots.

Cd concentrations in grains and straw in fields with lcd-kmt mutants

Field trials in three Cd-contaminated paddy fields showed that Cd concentrations in the grains (unpolished rice) of lcd-kmt1 and lcd-kmt2 were extremely low, near the limit of quantification (<0.01 mg kg⁻¹), whereas the Cd concentrations in the WT grains exceeded the maximum limit set by the Codex Alimentarius Commission (0.4 mg kg⁻¹). The straw Cd concentrations were also much lower in lcd-kmt1 and lcd-kmt2 than in the WT. These results reveal that the low-Cd- traits in the mutants were stable irrespective of different soil environments.

Agronomic traits of field grown lcd-kmt mutants

It was important to know if the lcd-kmt mutants grown in the paddy fields would exhibit excellent performance for grain Cd concentration without showing significant differences in agronomic traits to the WT Koshihikari. Field trials indicate that the mutant plants, lcd-kmt1 and lcd-kmt2, did not result in significant negative effects on the plant or grain morphology, eating quality, or grain yield; however, the shoot Mn concentrations of the lcd-kmt mutants did drastically decrease compared to those of WT. Rice is known to accumulate excess Mn without damage, and the Mn concentration in rice shoots can be more than an order of magnitude greater than those in soybean shoots. Presumably, rice may require less Mn for normal growth and can tolerate the excess Mn induced by the decreasing conditions in paddy soils. On the other hand, lcd-kmt3 exhibited negative effects on agronomic traits because it had earlier heading and smaller plant size than the WT. These results indicate that lcd-kmt1 and lcd-kmt2 can be used as
practical rice plants; \textit{lcd-kmt2} on the other hand, was registered as a rice variety with the name “Koshihikari Kan No. 1” by the Ministry of Agriculture, Forestry and Fisheries in Japan.

\textbf{Gene identification}

We developed an F$_2$ population by crossing Kasalath, an indica-type rice cultivar, with \textit{lcd-kmt1}, and then performed positional cloning of the gene(s) responsible for the decreased Cd uptake by \textit{lcd-kmt1}. The frequency distribution for the shoot Cd concentrations in the 92 M$_2$ seedlings did not differ significantly from a 1:3 low:high segregation ratio, suggesting that the low-Cd trait of \textit{lcd-kmt1} is controlled by a single recessive gene. Genetic mapping showed that the responsible gene was localized on the short arm of chromosome 7, and sequence analysis identified mutations of \textit{OsNramp5}, which encodes a natural resistance-associated macrophage protein. It has been reported that \textit{OsNramp5} is involved in Mn, Fe, and Cd transport in rice roots (Ishimaru et al., 2012; Sasaki et al., 2012). The cDNA and genomic DNA sequences of \textit{OsNramp5} revealed a single-nucleotide deletion in exon IX of \textit{lcd-kmt2} and a 433-bp insertion in the exon X of \textit{lcd-kmt1}. The inserted DNA sequence is identical to a sequence in mPingA1, a member of a class of miniature inverted-repeat transposable elements in rice. The \textit{OsNramp5} mutant transporter proteins failed to mediate uptake of Cd, Mn, and Fe in yeast, indicating a loss of function for these metal transporters in the cell membrane. According to these results, we drew a schematic diagram of the genetic and molecular mechanism for the decreased Cd uptake in the \textit{lcd-kmt} lines (Fig. 1). In Koshihikari, the roots can absorb Cd through the functional \textit{OsNramp5} protein. On the other hand, \textit{lcd-kmt} mutants are not able to absorb Cd, probably because of the alteration of protein structure of \textit{OsNramp5}. Therefore, the defective mutated transporter greatly decreases root Cd uptake, resulting in decreased Cd in the straw and grain.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic diagram of the genetic and molecular mechanism for decreased Cd uptake in the \textit{lcd-kmt} lines.}
\end{figure}
Development of genetic markers for breeding

DNA markers that detect polymorphism in the mutated genome region can be used to develop new cultivars with the low-Cd trait. We designed primer sets to amplify the mutated region and observed different patterns of DNA fragment amplification both between the WT and \( \text{lcd-kmt1} \) and between the WT and \( \text{lcd-kmt2} \) after FspI digestion (cleaved amplified polymorphic sequences marker). Figure 2 shows a scheme of maker-assisted breeding to develop new cultivars with low-Cd traits. The procedure is as follows: A low-Cd mutant is crossed with cultivar A, a parent for backcrossing, and the resultant F1 plant is backcrossed to cultivar A checking for the low-Cd gene using the DNA marker. After several backcrosses, the resultant BC\(_n\)F\(_1\) is self-pollinated and the BC\(_n\)F\(_2\) with homozygous for the mutant gene allele in the genetic background of cultivar A is selected. In Japan, we have launched a breeding program to change Japanese cultivars to the low-Cd type.

4) Phytoextraction

Necessary conditions for Cd-polluted paddy fields

Phytoextraction using hyperaccumulator plants has been proposed as a promising, environmentally friendly, low-cost technology to decrease the heavy-metal content of contaminated soils and has emerged as an alternative to engineering-based methods (Ebbs et al., 1997; McGrath et al., 2002). Hyperaccumulator plants can accumulate pollutants at high concentrations in their shoots and can grow in soils containing high concentrations of metals (Ebbs et al., 1997). Chaney et al. (2004) reported that some ecotypes of *Thlaspi caerulescens* in southern France showed high potential as a phytoextraction technology for low cost soil Cd remediation. However, *T. caerulescens* may not be suitable for large-scale phytoextraction.
because the plants are small and grow slowly, making them difficult to harvest mechanically (Ebbs et al., 1997). The Cd uptake efficiency of *T. caerulescens* in soils with relatively low levels of Cd pollution may also not be maintained in soils with more severe pollution (Brown et al., 1995). By using *T. caerulescens* for phytoextraction of low concentration Cd in soils, competition from weeds (never a problem in highly contaminated soils) needs to be controlled (Robinson et al., 1998). Moreover, culturing these hyperaccumulator species could be hampered by their susceptibility to certain diseases. For example, McGrath et al. (2000) reported that several *Thlaspi* species had been infected by diseases whose development was favored by prevailing humid and warm weather conditions. Because the typical weather conditions of Monsoon Asian summers are humid and warm, it may be difficult to introduce these species into Monsoon Asian paddy fields contaminated with low concentrations of Cd. To maximize the efficiency of phytoextraction, it is important to select a phytoextraction plant with a high Cd-accumulating ability that is also compatible with local mechanized cultivation techniques and weather conditions. Such a plant may yield more immediately practical results than a selection based solely on high tolerance to Cd.

Several phytoextraction studies have tested non-hyperaccumulator high-biomass plants such as Indian mustard (*Brassica juncea* L.) (Nanda Kumar et al., 1995; Ebbs et al., 1997), tobacco (*Nicotiana tabacum* L.) (Mench et al., 1989), industrial hemp (*Cannabis sativa* L.) (Linger et al., 2002), flax (*Linum usitatissimum* L.) (Angelova et al., 2004), vetiver grass (*Vetiveria zizanioides*) (Chen et al., 2000), poplar (*Populus spp.*) (Laureysens et al., 2005), and willow (*Salix spp.*) (Hammer et al., 2003). These plants can be cultivated in agricultural fields in Japan. However, rice is the staple crop in Japan, and its cultivation system is well established and highly mechanized. The use of an agricultural species adapted to the growing conditions of paddy fields is therefore a better alternative.

**Plant selection for Cd-polluted paddy fields**

Rice, soybean (*Glycine max* (L.) Merr.), and maize (*Zea mays* L.) are the major summer crops grown in paddy fields and in upland fields (fields under aerobic soil conditions) that have been converted from paddies in Japan. The cultivation systems for these crops are well established and highly mechanized. However, the study of phytoextraction using rice and soybeans has not yet been examined.

Rice (cv. Nipponbare and Milyang 23), soybean (cv. Enrei and Suzuyutaka), and maize (cv. Gold Dent) were grown on an Andosol and two Fluvisols with low concentrations of Cd pollution ranging from 0.83 to 4.29 mg Cd kg\(^{-1}\) for 60 days in pots (550 mL) in a greenhouse. Relative shoot Cd uptake was as follows: Gold Dent < Enrei and Nipponbare < Suzuyutaka and Milyang 23. Several soil Cd fractions (exchangeable, inorganically bound and organically bound) decreased the most after harvesting Milyang 23. Milyang 23 accumulated 10%–15% of the total soil Cd in its shoot. These values are much higher than those reported for *B. juncea* (0.09%) and *T. caerulescens* (0.06%) grown in soil containing 40 mg kg\(^{-1}\) of total Cd for 6 weeks in pots (Ebbs et al., 1997). The Milyang 23 rice is therefore promising for phytoextraction of Cd from paddy soils with low Cd pollution in aerobic soil conditions (Murakami et al., 2007).
Phytoextraction by rice capable of accumulating Cd at high levels

Previous research has shown that the Cd concentration in rice shoots grown under flooded (decreasing) soil conditions may be low, because Cd solubility under these conditions is lower than under oxidizing conditions (Kabata-Pendias and Pendias, 2001). Because shoot Cd uptake by rice plants equals the product of the dry weight (DW) and the Cd concentration of the rice shoots, maximizing shoot Cd uptake requires management practices that enhance both DW and Cd uptake by the rice shoot. The DW of rice shoots grown under flooded soil conditions is higher than that under oxidizing soil conditions during tillering (from transplantation to 30 days before panicle initiation (Takahashi, 1974). Therefore, the soils of all subplots were maintained under flooded conditions during tillering to maximize the DW of the rice shoots. Once the floodwater was drained from the subplots, the soils were maintained under oxidizing conditions until harvesting to maximize Cd accumulation by the rice shoots (“without irrigation after drainage”) (Murakami et al., 2009).

The total shoot Cd uptake by Indica Chokoukoku grown for 2 years (883 g ha⁻¹) was higher than 3-year grown Indica Moretsu (869 g ha⁻¹), Indica–Japonica Milyang 23 (638 g ha⁻¹), and Indica IR8 (532 g ha⁻¹) (Fig. 3). This 2-year shoot Cd uptake by Indica Chokoukoku from soil

![Fig. 3](image_url)

Fig. 3  Shoot and root Cd uptakes by indica-type rice cultivars capable of accumulating Cd at high levels and shoot Cd uptake by the japonica food rice cultivar. Means in the same year (shoot or root) are labeled with the same letter and do not differ significantly (p < 0.05, Tukey-Kramer’s HSD test). Error bars represent the standard error (n=2). Aki; Akitakomachi; IR, IR8; Mo, Moretsu; Mil, Milyang 23; Cho, Chokoukoku. J, Japonica; I, Indica; IJ, Indica-Japonica. Shoots were harvested in mid-October of 2004 to 2006. Residual roots were sampled in early May of 2007.
containing 1.63 mg kg$^{-1}$ of total Cd was higher than the uptakes by the hyperaccumulator T. caerulescens (540 g ha$^{-1}$ after 3 years of cultivation in soil with a total Cd content of 2.8 mg kg$^{-1}$) (Hammer and Keller, 2003), by willow Salix viminalis (170 g ha$^{-1}$ after 5 years of cultivation in soil with a total Cd content of 2.5 mg kg$^{-1}$) (Hammer et al., 2003), and by the poplar (Populus) clone Balsam Spire (57 g ha$^{-1}$ after 2 years of cultivation in soil with a total Cd content of 0.75 mg kg$^{-1}$) (Laureysens et al., 2005). In contrast, Cd uptake by the residual roots of Indica Chokoukoku was lower than those of the other indica and indica-japonica rice cultivars. Cadmium in the residual roots may be released gradually into the soil as the roots are decomposed by soil organisms. Because phytoextraction involves harvesting plant shoots that have taken up toxic elements from the soil and removing harvestable material from the contaminated fields, plants such as Indica Chokoukoku, with high shoot Cd uptake and low root Cd uptake, are ideal for phytoextraction. Moreover, rice plants can be cultivated continuously (De Datta, 1981). The shoot DWs of the four indica and indica-japonica rice cultivars did not decrease, even after two or three continuous cultivations without irrigation after drainage, indicating that growth damage from continuous cultivation and the presence of toxic metals in the soil did not occur. This characteristic of rice is also useful for phytoextraction.

The exchangeable, inorganically bound, organically bound, and total soil Cd concentrations were lowest in the Indica Chokoukoku subplot, despite the fact that this cultivar was grown for only 2 years. This suggests that this cultivar can take up Cd more efficiently than the other rice cultivars from the more resistant (inorganically and organically bound) fractions, as well as from the more bioavailable (exchangeable) fraction. This uptake capability equaled that of the hyperaccumulator T. caerulescens when pot-grown (Hammer and Keller, 2002). The Cd uptake by the residual roots of Indica Chokoukoku (29.5 g ha$^{-1}$) corresponded to only 0.02 mg kg$^{-1}$ of soil Cd. Even allowing for the return of this root Cd to the soil by microbial decomposition, the total soil Cd concentration in the Indica Chokoukoku subplot was 38% less than the mean value in the subplots with no plants (a reduction from 1.63 to 1.01 mg kg$^{-1}$). This reduction in total soil Cd concentration by the 2-year grown Indica Chokoukoku was higher than the reduction by the 3-year grown hyperaccumulator T. caerulescens (by 15% of the total soil Cd, assuming that this plant took up Cd from soil to a depth of 15 cm with a bulk density of 0.85 mg m$^{-3}$) (Hammer and Keller, 2003).

The Japonica food rice cultivar Yumesayaka grown after phytoextraction by the four indica and indica-japonica rice cultivars and in the subplots without phytoextraction showed normal growth. The average grain yields were Japonica Yumesayaka grown in the four subplots after phytoextraction and in the no plant subplot (5.1 mg ha$^{-1}$) was similar to those of Japonica food rice cultivars in Japan in 2007 (5.2 mg ha$^{-1}$) (MAFF, 2008). The grain Cd concentrations of Japonica Yumesayaka grown after 2 years of phytoextraction with Indica Chokoukoku were decreased by 47% (to 0.54 mg kg$^{-1}$) of that of the same rice cultivar grown without phytoextraction (1.02 mg kg$^{-1}$).

Phytoextraction with Indica Chokoukoku rice grown for 2 years without irrigation after drainage removed 883 g Cd has, decreased the total soil Cd content by 38%, and decreased the grain Cd content in subsequently grown Japonica food rice by 47% without decreasing yield.
These results suggest that phytoextraction with Indica Chokoukoku can remove Cd from paddy fields polluted with low to moderate levels of Cd and decrease the grain Cd concentration of Japonica food rice cultivars to below the Codex standard within a reasonable time frame. This approach will help decrease the risk of Cd pollution for rice in paddy fields.

**Development of a rice cultivar for Cd-phytoextraction**

A high-Cd-accumulating rice cultivar seems to be a good method to extract Cd from Cd-polluted paddy fields. Uraguchi et al. (2009) found that the indica rice cultivar “Jarjan” had the highest Cd accumulation in shoots in the world rice core collection when grown in Cd-polluted soil. Abe et al. (2011) found the responsible gene locus involved in the high Cd accumulation of Jarjan and designated the locus $qCdp7$ (a QTL potentially useful for Cd-phytoextraction on chromosome 7). The gene underlying the effect of $qCdp7$ is probably a mutation of $OsHMA3$, which encodes a tonoplast-localized Cd transporter; Jajan fails to sequester Cd into its root vacuoles via $OsHMA3$, resulting in increased Cd accumulation in its shoots (Ueno et al., 2011). Although the Jarjan allele of $qCdp7$ can contribute to decreasing soil Cd contamination, this cultivar has several negative traits and is sensitive to shattering and lodging unfavorably in the Japanese mechanized cropping system. Therefore, we produced a mutant rice resistant to shattering and lodging by gamma-ray irradiation of the seeds of Jarjan. The selected mutant displayed lodging as resistant as the japonica cultivar Koshihikari because this trait was improved in the semi-dwarf without decreasing its yield (Fig. 4). The trait of shattering was improved as well, and high Cd accumulation was maintained in the mutant because of the presence of the Jarjan allele $qCdp7$. The mutant was given the name “Phyreme CD No. 1” in the rice variety registration system of Japan and a national project is on-going to verify the effectiveness of Cd-phytoextraction using this cultivar.

![Fig. 4 Plant morphologies of Jarjan, Koshihikari, and Phyreme CD No1 grown in the paddy field.](image-url)
3. Soil Washing

Soil washing involves the use of chemical reagents to extract hazardous metals from soil into an aqueous solution (Elliott and Herzig, 1999); it is conventionally performed ex situ using appropriate equipment. In situ soil washing is usually called “soil flushing”. The phrase “soil washing” is therefore used consistently in this section to avoid confusion with soil flushing. Soil washing techniques offer a great advantage over soil flushing because they remove Cd from contaminated soils with high efficiency. However, soil washing has been considered difficult to apply directly to agricultural land because wastewater discharged during the process of soil washing might pollute the surrounding environment, including agricultural canals, neighboring agricultural fields, and groundwater. However in paddy fields, just below the subsurface layer are an impervious hardpan that hinders the vertical movement of water. During soil washing, the wastewater thus stays in the surface soil and hardly penetrates into subsoil layers and groundwater; therefore, where necessary in paddy fields, an in-situ soil-washing methodology should be used to take advantage of this unique characteristic.

The methodology of in situ soil washing of paddy fields must meet the following criteria (Makino et al., 2006; 2007):

1. The wash chemicals must remove Cd with high efficiency and with minimal environmental impact on the paddy field.
2. The soil-wash system must be cost-effective and environmentally sound.
3. The soil washing must not impair soil fertility; healthy plant growth should follow the wash treatment.
4. The sustainability of the effect of the soil washing should be confirmed.

Makino and his team (Makino et al., 2006; 2007) have developed a new soil washing methodology combined with on-site wastewater treatment that completely satisfies these four requirements. This methodology is discussed in section 3, 1).

1) Screening of washing Chemicals and Mechanism of Cd Extraction

Chelating agents, neutral salts, and strong acids have been used to solubilize metals during soil washing. In particular, ethylenediamine tetraacetic acid (EDTA) has been commonly used because it efficiently removes Cd from contaminated soils (Nakashima and Ono, 1979; Abumaizar and Smith, 1999; Zeng et al., 2005). EDTA, however, remains in the environment for a long time (Tandy et al., 2004). Some scientists have therefore used more biodegradable chelating agents instead of EDTA (Mulligan et al., 1999; Hong et al., 2002; Tandy et al., 2004; Chang et al., 2005; Kantar and Honeyman, 2006; ). If the agents are biodegradable, however, the cost is higher than is the case if non-degradable or less degradable counterparts are used.

Makino et al. (2006) have noted that calcium chloride (CaCl₂) is one of most appropriate soil-washing chemicals for Cd-contaminated paddy soils on the basis of its Cd-extraction efficiency, cost-effectiveness, and relatively low environmental impacts. The high efficiency with which
CaCl\textsubscript{2} extracts Cd from soil is mainly attributable to the high selectivity of Ca for soil adsorption sites compared with monovalent cations, the concurrent lowering of the solution pH due to hydrolysis of exchangeable Al, and the formation of Cd-Cl complexes. Makino et al. (2006) have also noted that hydrochloric acid (HCl), nitric acid (HNO\textsubscript{3}), and disodium EDTA extract more Cd from soil than neutral salts. However, disodium EDTA is poorly suited for soil washing for practical purposes: it is persistent in the environment, and its cost is relatively high. Both HCl and HNO\textsubscript{3} can cause serious soil acidification if the pH-buffering capacity of the soil is low.

Makino et al. (2006) found that ferric chloride (FeCl\textsubscript{3}) extracted nearly as much Cd as did HCl, HNO\textsubscript{3}, and disodium EDTA from three soils (two Fluvaquents and an Epiaquept). Iron is a major soil constituent and is less environmentally harmful than the other three chemicals. In addition, FeCl\textsubscript{3} is less expensive and easier to handle than both HCl and disodium EDTA. Ferric chloride was thus considered to be a promising washing chemical. The Cd-extraction capacity of FeCl\textsubscript{3} was therefore compared with that of other metal salts to elucidate the mechanism by which FeCl\textsubscript{3} extracted Cd. The proportion of total soil Cd extracted by the washing chemicals (i.e., the Cd extraction efficiency) increased in the following order in all three soils: Mn salts ≤ Zn salts << ferric Fe salts. Efficiencies ranged from 4–41%, 8–44%, and 24–66%, respectively. The amount of Cd extracted was negatively correlated with the extraction pH, the suggestion being that extraction pH plays an important role in determining Cd extraction efficiency.

When metal salts are added to soils, the dissociated metal cations may form hydroxide precipitates with the release of protons (H\textsuperscript{+}) according to the following equations (hydrolysis):

\begin{align*}
\text{MmAn} & = mM^{m+} + nA^{n-} \quad (3) \\
M^{m+} + nH_2O & = M(OH)_n + nH^+ \quad (4) \\
K^\circ m & = [H^+]^n/[M^{m+}] \quad (5)
\end{align*}

where MmAn denotes a metal salt, M a metal cation (Fe, Zn, or Mn), and A an anion (Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, or SO\textsubscript{4}\textsuperscript{2-}); m and n represent the charges of the anion and cation, respectively; K\textsuperscript{m} denotes the equilibrium constant (expressed in terms of activities) for metal M\textsuperscript{m+} in Eq. 4. The value of K\textsuperscript{m} equals 2.88 \times 10\textsuperscript{-4}, 3.31 \times 10\textsuperscript{-13}, and 6.46 \times 10\textsuperscript{-16} for Fe\textsuperscript{3+}, Zn\textsuperscript{2+}, and Mn\textsuperscript{2+}, respectively (Lindsay, 1979).

The precipitation of the metal hydroxide (hydrolysis of the metal ion) generates H\textsuperscript{+} to an extent that depends on K\textsuperscript{m}, and the protons generated in Eq. 4 decrease the extraction pH. Based on the theoretical relationship between pH and the activity of ferric iron when the iron hydrolysis reaction is at equilibrium (calculated using Eq. 5 and the K\textsuperscript{m} of 2.88 \times 10\textsuperscript{-4}), the formation pH of ferric hydroxide will be around 2, which is much lower than the original pH of the three soils.

Because the K\textsuperscript{m} for the Fe-hydrolysis is many orders of magnitude higher than the K\textsuperscript{m} for the other two metals, the Fe-hydrolysis is associated with a greater decrease in soil pH than is the case for the other two metals. Thus a driving force for Cd extraction by FeCl\textsubscript{3} is proton release, which results in a sharp decrease in soil pH. In another study, Cd was highly mobile under the oxidizing and acidic conditions in these soils (Kabata-Pendias, 2000). Heavy metal
solubilization was greatly enhanced by acidification, and at pH 1.3 more than 80% of the total Cd in the soil was solubilized (Dube and Galvez-Cloutier, 2005). The results obtained in that study support the use of iron salts to efficiently remove Cd from soil via soil washing.

The Cd extraction efficiency of metal chlorides was greater than that of the corresponding metal sulfates and nitrates in all soils. In a Fluvquent soil, extraction efficiencies decreased in the following order: chlorides > nitrates ≈ sulfates with efficiencies from 41–75%, 14–63%, and 26–62%, respectively. The results were similar for the other two soils. To examine the factors that resulted in the difference of the extraction efficiencies of the metal salts, Makino et al. (2008) used Visual MINTEQ software to estimate the relative abundance of dissolved Cd species in a 100 mmolc L-1 iron salt solution (Gustafsson, 2004). Cd–Cl complexes such as CdCl⁺ and CdCl₂ (aq) accounted for 80% of the total dissolved Cd in the soil at 100 mmolc L⁻¹ FeCl₃ versus 33% for Fe₂(SO₄)₃ and 9% for Fe(NO₃)₃. Similar trends were observed for the other metal salts and soils. Cadmium has a high capacity to form complexes with anions such as Cl⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻, organic acids, and fulvic acid (Traina, 1999; Kunhikrishnan et al., 2012). Doner (1978) reported that Cd was leached more rapidly in the presence of Cl⁻ than in the presence of ClO₄⁻. Sakurai and Huang (1996) have shown that the rate of desorption of Cd from a montmorillonite was greater with KCl than with KNO₃. Smolders and McLaughlin (1996) have suggested that high concentrations of Cl⁻ in saline soils might increase plant uptake of Cd, either by enhancing mass transport of Cd or by enhancing uptake of the CdCl⁺ complex by plant roots. Accordingly, the formation of stable Cd–Cl complexes could inhibit resorption of the extracted Cd onto adsorption sites on the surface of the soil particles. This mechanism of inhibition improves the efficacy of extraction with FeCl₃ compared to that with Fe₂(SO₄)₃ and Fe(NO₃)₃ because the ratio of Cd complexes to total dissolved Cd is high in extracts with chloride salts.

2) Development of a Soil Washing (Soil Flushing) System for Paddy Fields

The soil-washing procedure developed by Makino et al. (2007) consisted of three steps: (1) chemical washing with appropriate chemical solutions, such as CaCl₂ and FeCl₃ to extract Cd from soils, followed by (2) water washing to eliminate the remaining chemicals, and (3) on-site treatment of the wastewater by a portable purification apparatus with a chelating material (Fig. 5). In a field study, a part of the paddy field was bound with plastic boards, which were partially buried at the edges of the paddy field so that the upper two-thirds of each board remained above the ground surface. This boundary provided containment for additional water and chemicals in the paddy field.

The flushing chemical was applied to the bounded experimental field, followed by the addition of agricultural water, creating a soil-solution ratio of 1:1.5 to 1:2. The soil suspension was mixed using a tilling machine until it turned into a slurry. It is important to mix the soil suspension thoroughly, because if the structure of soil clods is maintained, the diffusion of the washing chemical into the clods will likely be a rate-controlling factor for the extraction of soil-Cd. The soil suspension was allowed to rest after the mixing, and then the Cd-containing supernatant of the slurry was drained off as wastewater and sent to the wastewater treatment system (Makino et al., 2007).
The Cd concentrations in the treated wastewater were below the Japanese environmental quality standard (0.01 mg Cd L⁻¹), demonstrating that the in situ treatment system treated the wastewater as expected. The Cl concentration was <500 mg L⁻¹ after the water washes; this concentration is the threshold value for healthy rice crops.

The concentration of exchangeable Cd was significantly decreased after CaCl₂ and little changed after FeCl₃ washing, but the weakly acid-soluble Cd form decreased substantially during the FeCl₃ washing. Although the exchangeable Cd increased with the decreasing soil pH caused by the washing treatment, adjusting the pH to the initial pH by the addition of lime could decrease the level of exchangeable Cd concentration and maintain it at this level after the washing.

Soil pH values were significantly decreased after the washing treatment. Although electrical conductivity increased, it did not reach a level that would affect the growth of rice plants. Exchangeable Mg and K decreased because of the soil washing. The Mg and K deficiencies were corrected by applying fertilizers to the washed soil, therefore restoring the Mg and K concentration in the soil during the growth period. Total carbon and total N concentrations changed little. Although the extraction pH became very acidic with the application of FeCl₃, the amount of soil Al released was <1% of the total soil Al, indicating that the in situ soil treatment is unlikely to cause critical soil damage such as clay mineral destruction.

Soil washing considerably decreased the Cd concentrations in the rice grains. The reduction rates of unpolished rice after CaCl₂ and FeCl₃ washings were approximately 40% and 80%, respectively. These results proved the efficiency and effectiveness of the soil washing method for remediation of Cd-contaminated paddy fields.

**Fig. 5** Conceptual diagram of on-site soil washing.
4. Dynamics of Arsenic in Agricultural Fields and Countermeasures to simultaneously decrease As and Cd in Rice Grains

1) Bioavailability of Arsenic in Soils and its Uptake by Crops

It is well known that damage by arsenic (As) tends to occur more in paddy rice than in other upland crops. In the 1970s and 1980s, the mechanism of As damage to paddy rice and countermeasures for paddy rice fields were clarified by Koyama (1975), Koyama et al. (1976), Koyama and Shibuya (1976), Yamane et al. (1976), and Yamane (1979, 1989). Koyama and Shibuya (1976) conducted a pot experiment of paddy rice with As-contaminated soils and found a significant, negative correlation between 1-M HCl-soluble As in soil and brown rice yield. Countermeasures for paddy rice to prevent As damage were proposed by Yamane (1979), who suggested that the As-contaminated soils should be maintained in an oxidative state to suppress the dissolution of As. Ishizuka and Tanaka (1962) reported that 60%–80% of the total As content accumulated in the roots of paddy rice. Subsequently, Yamane et al. (1976) and Yamane (1989) reported that 90% of the total content of As accumulated in the roots. In addition, X-ray microanalysis of root sections revealed that most As in the roots was distributed at the root surface with Fe (Yamane, 1989).

As is highly mobilized when paddy soil is flooded, causing an increased uptake of As by rice. Yamaguchi et al. (2011) investigated factors controlling soil-to-solution partitioning of As under anaerobic conditions. Changes in As and iron (Fe) speciation because of flooded incubation of two paddy soils (soils A and B) were investigated by HPLC/ICP-MS and XANES. The flooded incubation resulted in a decrease in Eh, a rise in pH, and an increase in the As(III) fraction in the soil solid phase of up to 80% of the total As in the soils. The solution-to-soil ratio, R(L/S), of As(III) and As(V) increased with pH because of the flooded incubation. The R(L/S) for As(III) was higher than that for As(V), indicating that As(III) was more readily released from the soil to the solution than was As(V). Despite the small differences in As concentrations between the two soils, the amount of As dissolved by anaerobic incubation was lower in soil A. With the development of anaerobic conditions, Fe(II) remained in the soil solid phase as the secondary mineral siderite, and a smaller amount of Fe was dissolved from soil A than from soil B. The dissolution of Fe minerals rather than the redox reaction of As(V) to As(III) explained the different dissolution amounts of As in the two paddy soils. Anaerobic incubation for 30 days after the incomplete suppression of microbial activity caused a drop in Eh. However, this decline in Eh did not induce the transformation of As(V) to As(III) in either soils solid or solution phases, and the dissolution of As was limited. Microbial activity was necessary for the reductive reaction of As(V) to As(III) even when Eh reached the condition necessary for the dominance of As(III). Ratios of released As to Fe from the soils decreased with incubation time during both anaerobic incubation and abiotic dissolution by sodium ascorbate, suggesting that a larger amount of As was associated with an easily soluble fraction of Fe (hydr) oxide in amorphous phase and/or smaller particles.

Elevated As concentrations in rice and the soil solution result from changes in soil redox conditions, influenced by water management practices during rice cultivation. Microscale
changes in redox conditions from the rhizosphere to the soil matrix affect As speciation and Fe-plaque deposition. To focus on the rhizosphere environment, Yamaguchi et al. (2014) observed the microscale distribution and speciation of As around the rhizosphere of paddy rice using X-ray fluorescence mapping and X-ray absorption spectroscopy. When the soil matrix was anaerobic during rice growth, Fe-plaque did not cover the entire root, and As(III) was the dominant As species in the soil matrix and rhizosphere. Draining before harvest led the conditions to shift to aerobic. Oxidation of As(III) to As(V) occurred faster in the Fe-plaque than in the soil matrix. As was scavenged by iron mottles originating from the Fe-plaque around the roots. The ratio of As(V) to As(III) decreased toward the outer-rim of the subsurface Fe mottles where the soil matrix was not completely aerated. These results provide direct evidence that speciation of As near rice roots depends on spatial and temporal redox variations in the soil matrix.

2) Effects of Water Management on Arsenic Content, Cadmium Content and Arsenic Speciation in Rice Grains

When a paddy field is flooded and the soil is in a reducing condition, cadmium (Cd) in the soil combines with sulfur (S) to form CdS, which has a low solubility in water. However, when the field is drained and the soil is in an oxidative condition, CdS is converted into CdSO₄, which is soluble in water.

The effects of water management on levels of Cd and As in rice were investigated. Flooding increased As concentrations in rice grains, whereas aerobic treatment increased the concentration of Cd. Flooding for 3 weeks before and after heading was most effective in decreasing grain Cd concentrations, but this treatment increased the As concentration considerably, whereas aerobic treatment during the same period was effective in decreasing As concentrations but increased the Cd concentration markedly. Concentrations of dimethylarsinic acid (DMA) in grains were very low under aerobic conditions but increased under flooded conditions. DMA accounted for 3%–52% of the total As concentration in grain grown in soil with a lower As concentration and 10%–80% in soil with a higher As concentration (Arao et al., 2009a).

When rice was grown under flooded conditions after the heading stage, DMA amendment to the soil resulted in higher DMA concentrations in brown rice and rice straw. In the solution culture, not only DMA amendment but also MMA or arsenite amendment increased the DMA concentrations in brown rice and rice straw. DMA was detected in the solution amended by MMA or arsenite with young rice plants. When the solution included the antibacterial agent chloramphenicol, DMA concentration in the solution decreased dramatically. When just the soil was incubated with MMA or arsenite, only a slight amount of DMA was detected in the soil. These results suggest that rice rhizosphere associated bacteria are involved in the formation of DMA in brown rice (Arao et al., 2011a).

A unique bacterium responsible for As methylation was isolated from the rice rhizosphere. The strain GSRB54 (the genus Streptomyces) has a strong ability to methylate As. In addition, DMA was detected in the shoots of rice grown in a liquid medium inoculated with GSRB54 and containing As(III). Because Streptomyces are generally aerobic bacteria, Kuramata et al. (2015)
speculate that the strain GSRB54 inhabits the oxidative zone around roots of paddy rice and is associated with DMA accumulation.

Ishikawa et al. (2012) produced a japonica rice cultivar (Koshihikari Kan No. 1) with nearly undetectable levels of Cd in its grains by means of mutant breeding. This low-Cd rice cultivar enables the simultaneous reduction of As and Cd in rice grains under water saving conditions (Ishikawa et al., 2016a).

3) The Genetic Diversity of Arsenic Accumulation in Rice

As accumulation and speciation in the major cultivars currently grown in Japan was examined. As levels among Japanese cultivars may not influence dietary As exposure, because there is little genotypic difference in the accumulation of inorganic As (Kuramata et al., 2011).

The genetic diversity in As accumulation and As speciation in rice grains was investigated using WRC comprised of 69 accessions grown over a 3-year period. There was a 3-fold difference in the grain As concentration of WRC. Concentrations of total-As, inorganic As, and DMA were significantly affected by genotype, year, and genotype-year interaction effects. Among the WRC accessions, Local Basmati and Tima (indica–type) were identified as cultivars with the lowest stable total-As and inorganic As concentrations. Using an F2 population derived from Padi Perak (a high-DMA accession) and Koshihikari (a low-DMA cultivar), two QTLs on chromosome 6 and one QTL on chromosome 8 that were responsible for variations in the grain DMA concentration were identified. Approximately 73% of the total phenotypic variance in DMA was explained by these three QTLs (Kuramata et al., 2013).

4) Application of Soil Amendments on Arsenic Solubility in Soils and Availability for Rice Plant

In addition to water management, the application of soil amendments is one strategy to attenuate As in rice plants. There are many possible As-insolubilizing materials such as clays, layered double hydroxides (LDHs), Al oxides, Mn oxides and Fe-type adsorbents (e.g., Fe oxides, zero-valent iron (Mohan and Pittman, 2007)). Many examinations of these materials have been carried out to insolubilize As in water systems and heavily contaminated soils (Boisson et al., 1999; Yang et al., 2005). Iron-type adsorbents, some of them indigenously existing in soils, are generally considered promising. However, few studies have focused on slightly contaminated paddy soils, which pose a possible risk of producing rice that exceeds the permitted concentration of As, especially where flooded (anaerobic) cultivation is conducted to decrease Cd in rice.

Therefore, we tested some As-insolubilizing materials to decrease dissolved As under long-term flooded incubation (Suda et al., 2015). As expected, the addition of Fe oxides (ferrihydrite and Al-substituted ferrihydrite) effectively insolubilized As in the soils, however, the effect gradually diminished with time. The additions of LDH and magnesium oxide successfully insolubilized As in one soil, but did not in another. Moreover, the addition of the precipitate of a polysilicate-iron (PSI) solution insolubilized As in soils as much as ferrihydrite did. Because PSI precipitate is a major component in certain types of water-treatment residue (WTR), we conducted a pot experiment to examine the effects of a PSI-containing WTR (PSI-WTR) on
dissolved As in flooded soils and As uptake by rice plants (*Oryza sativa* L.) (Suda et al., in press). Dissolved As remained less in the PSI-WTR-treated soils than in the control soils during the cultivation period, possibly because of the adsorption of As on ferrihydrite-like components in PSI-WTR. Simple liner regression analyses showed that As in the soil solution and rice tissue (grains, husks, and straws) and As uptake by the rice plant are negatively correlated with PSI-WTR application rates (0, 5, 10, and 20 t ha$^{-1}$). Total As uptake was 16.5%–32.0% lower in rice shoots grown in PSI-WTR-treated soils than in control soils. Therefore, PSI-WTR is possibly a practical amendment to attenuate As in rice at low cost.

The application of silicate amendments is another possible strategy to restrict As uptake by rice. Although dissolved Si decreases As adsorption onto Fe oxides through Si adsorption and subsequent polymerization (Swedlund and Webster, 1999), strong negative correlations ($r = -0.9$ to $-0.99$) between dissolved Si in soil solution and As concentration in rice plants have been reported (Bogdan and Schenk, 2008). It is possible that As(III) is transported by the same pathways as Si (Ma et al., 2008), and dissolved Si inhibits root absorption of As (Guo et al., 2005). Large applications of silicate (20 g of silica-gel per kg soil) increased dissolved As in soils, and As uptake by rice plants was decreased (Li et al., 2009; Liu et al., 2014). However, it is not clear whether or not the usual application rate of Si amendments is sufficient to decrease As uptake by rice.

Organic amendments potentially both solubilize and insolubilize As in soils through various mechanisms. Some studies show that organic amendments decreased the uptake of As by rice plants (Rahaman et al., 2011), whereas contrasting results have also been reported (Norton et al., 2013).

The effect of amendment on As solubility in soils and uptake by rice plants could be determined by many factors such as soil properties and water management. Systematic and comprehensive studies are required to evaluate the benefits (or risks) of soil amendments on As uptake by rice plants. We have confirmed the suppressive effect of some iron materials on As concentration in soil solution and rice grain at five paddy fields having various soil properties (Makino et al., 2016). In future, we should focus on industrial by-products and wastes, because cost efficiency is one of the most important considerations in countermeasures for As-related problems in agriculture.

5) Biogeochemical Changes and Rice Uptake of Aromatic Arsenicals in Agricultural Soils

Chemical warfare agents containing aromatic arsenicals (AAs) such as Clark I (diphenylchloroarsine) were produced mainly as vomiting or vesicant agents during World War I and II. After World War II, these agents and other chemical weapons were abandoned by Europe, China, Japan, and other countries and dumped at sea or buried in the earth. Their constituent compounds can be metabolized in groundwater, soil, and sediments via hydrolysis and oxidation, resulting in the formation of diphenylarsinic acid (DPAA) and other AAs. In 2002, the inhabitants of the Kizaki region of Kamisu in Ibaraki Prefecture, Japan, exhibited uncommon clinical symptoms of the central nervous system, and in 2003, DPAA, bis(diphenylarsine) oxide (BDPAO), and phenylarsonic acid (PAA) were detected in the groundwater consumed by
Kamisu inhabitants. The origin of DPAA in the groundwater of Kizaki is unclear; however, DPAA that was used to synthesize diphenylchloroarsine may have been abandoned in this region. In 2004, DPAA and methylphenylarsenic acid (MPAA) were detected in paddy rice in Kamisu.

The uptake of AAs in agricultural soils by rice was therefore investigated (Baba et al., 2008; Arao et al., 2009b). MPAA was detected in brown rice grown in contaminated soil. Dimethylphenylarsine oxide (DMPAO) and methyldiphenylarsine oxide (MDPAO) were detected in straw, but not in grains, grown in contaminated soil, in which PAA and MPAA concentrations decreased and DMPAO concentration increased under flooded conditions. The concentrations of PAA and MPAA, however, remained unchanged under upland conditions. DMPAO was detected in the straw of rice grown in PAA-amended and MPAA-amended soils but was not detected in that grown in a PAA-added or MPAA added solution culture. On the other hand, MDPAO was detected in the straw of rice grown in DPAA-amended soil but not in that grown in a DPAA-added solution culture. Therefore, MPAA and DPA were methylated, not only in the rice plant but also in the soil under flooded conditions. Dephenylated products were detected in the straw grown in AAs-added solution cultures, whereas demethylated products were not detected. DMPAO and MDPAO absorbed by the shoots were retained, and MPAA and DPAA absorbed by the shoots were translocated to the grains more easily than other AAs.

The effects of activated charcoal (AC) amendment on levels of AAs in rice and soybeans were investigated (Arao et al., 2011b). The most abundant AA in rice grains and soybean seeds was MPAA. MPAA concentration in rice grains was significantly reduced to 2–3% in 0.2% AC treated soil compared to untreated soil in the first year of rice cultivation. In the second year, MPAA concentration in rice grains was significantly reduced to 15% in 0.2% AC treated soil compared to untreated soil. MPAA concentration in soybean seeds was significantly reduced to 44% in 0.2% AC treated soil compared to untreated soil. AC amendment was therefore effective in decreasing AAs in rice and soybeans.

Maejima et al. (2011a) investigated the transformation and fate of DPAA during incubation in two types of soils (Fluvisol and Andosol) under both aerobic and anaerobic conditions. DPAA was transformed into MDPAO by methylation only under anaerobic conditions. Under both aerobic and anaerobic conditions, DPAA was degraded to PAA by dephenylation, and PAA was subsequently methylated to form MPAA and DMPAO. The degradation of DPAA in Andosol was less extensive than in Fluvisol. In autoclaved soil under anaerobic conditions, DPAA underwent little degradation during the 24 weeks of incubation. In unautoclaved soils, however, the concentration of DPAA clearly decreased after 24 weeks of incubation, indicating that DPAA degradation was driven by microbial activity. We therefore proposed a scheme for the transformation and fate of DPAA in soils.

Maejima et al. (2011b) also investigated the adsorption and mobility of AAs in two types of Japanese agricultural soils in batch and column leaching experiments. The amounts of AAs adsorbed onto a Fluvisol (a sandy loam) and an Andosol (a light clay) decreased in the order of PAA > MPAA > DPAA > MDPAO > DMPAO. The amounts of all AAs adsorbed onto the Andosol, which had more amorphous minerals and organic carbon, were higher than those
adsorbed onto the Fluvisol. The adsorbability of AAs increased with both increasing arsenate proportion and decreasing hydrophobicity. This result suggests that the mechanisms of adsorption of AAs onto soil are due more to ligand exchange reactions and less to hydrophobic interactions. The mobility of MDPAO and DMPAO was higher than that of PAA and MPAA, and all AAs were less mobile in Andosol than in Fluvisol.

5. Conclusions

Risk management of Cd and As contamination in rice grains is a priority issue and a great challenge for the population of Monsoon Asia. Some risk alleviation methods have been introduced in this chapter. Conventional countermeasures, such as soil dressing and water management, are highly effective to decrease Cd in rice grains. Soil dressing is, however, expensive and long-term flooding can release As from soils under the low redox conditions, indicating that the relationship between Cd and As requires a “risk trade-off.” Low-Cd-accumulating rice varieties can be used to minimize the Cd reaching the food chain. Phytoremediation, which is relatively inexpensive, has been proven effective in remediating metal(loid)s-contaminated sites, including those with Cd. Soil washing is a confirmed method to decrease Cd concentration in soils, while it requires a relatively high cost. We need to integrate water management, soil amendment and low-Cd/As-accumulating cultivars to simultaneously decrease Cd and As in rice grains while considering the trade-off relationship between the two. A similar risk trade-off is found between methane release from paddy fields and manure application, because of the promotion of decreasing conditions in the paddy soil by manure application. This means tri-lemma dynamics among Cd, As and methane in paddy fields. Therefore, many factors need to be balanced. To find the optimal solution, we have to accumulate scientific knowledge on the dynamics of the various substances in soils and develop integrated countermeasure.

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References


Hammer, D. and Keller, C., 2002. Changes in the rhizosphere of metal-accumulating plants evidenced by...


-October of 2004 to 2006. Residual roots were sampled in early May of 2007.