Management Strategies for Heavy Metals to Secure the Crop Safety in Korea

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Abstract

There are growing public concerns over crop and food safeties due to the elevated levels of heavy metals grown in contaminated soil. Heavy metals are classified as the chemical harmful risks for crop and food safety. With implementation of GAP, crop safety is controlled by many regulatory options for soil, irrigation water and fertilizers. Any attempt to retard the metal uptake by crops may be the best protocol to secure crop and food safety. This article reviews the management strategies for heavy metals in view of crop safety in Korea and demonstrates results from the field experiments to retard metal translocation from soil to crops by using chemical amendments and soil layer management methods. Major source of soil pollution by heavy metals has been related with mining activities. Risk assessment revealed that rice consumption and groundwater ingestion in the abandoned mining areas were the major exposure pathways for metals to human and the heavy metal showed the toxic effects on human health. Chemical amendments such as lime and slag retarded Cd uptake by rice (*Oryza sativa* L.) by increasing soil pH, lowering the phytoavailable Cd concentration in soil solution, immobilizing Cd in soil and converting the available Cd fractions into non-available fractions. The soil layer management methods decreased the Cd uptake by 76% and Pb by 60%. Either reversing the surface layer with subsurface layer or immobilization of metals with layer mixing with lime was considered to be the practical option for the *in-situ* remediation of the contaminated paddy soils. Combination of chemical soil amendments and layer management methods was efficient to retard the metal bioavailability and thus to secure crop safety for heavy metals. This protocol seems to be cheap, relatively easy to practice and practical in the agricultural fields. However, a long term monitoring work should be followed to verify the efficiency of this protocol.

Key words : Chemical amendments, Crop safety, Heavy metals, remediation, soil layer management

Introduction

Arable lands in nearby industrial and urban areas in Korea have become contaminated with various sources of contaminants including heavy metals, pesticides, nutrients and hazardous organic compounds, etc. There is growing concern over crop and food safety because these contaminants can be bioaccumulated in the crops (Yang et al., 2007; Kim et al., 2007). Translocation of these contaminants into crops can be a threat to human health through food chain. Soil quality is thus considered as an important environmental issue related with human health because soil can produce food and fiber as well as maintain the ecosystem health.

The extensive monitoring results in Korea reveal that concentrations of heavy metals in arable lands have increased slightly in last several decades but are mostly below the regulatory levels designated by the Soil Environment Conservation Law (SECL), unless there exist evident anthropogenic sources of contaminants (SGIS, 2007; Yang et al., 2000). Major sources of heavy metals causing soil contamination in Korea are mostly derived, directly or indirectly, from the mining sites, industrial or domestic wastewater, solid wastes, and sewage sludge (Yang et al., 2007).

Bioavailability is defined as the extent to which living receptors are exposed to contaminants in soil (Feng et al., 2005). Bioaccumulation of Cd in rice from the contaminated paddy field becomes major crop safety issues since rice is staple crop in Korea. Metal bioavailability depends in general on soil's factor, plant's factors and metal's factor (Basta et al., 2005; Sparks, 2003). Soil's factors include soil solution, supply mechanism and buffering capacity. These are integrated soil properties which are closely related with individual chemical, physical and biological properties of soils. Plant's factors are mostly related with plant species and root morphology and physiology (type, age, number, depth etc.). Metal's factor is governed by metal species present in soil which are relied on the chemical and physical conditions of soils.

A number of factors affect the level of metal in crops: soil, plant, climate, water, atmospheric deposition and degree of maturity of crop at time of harvesting, etc. Among these, the soil properties are one of the most important factors in determining the level of metals in crops and foods. Heavy metal contamination of arable soils can thus pose a long-term environmental problem and is not without human health implications (Muchuweti et al., 2006).

In Korea, metal concentrations in crops and foods are regulated by the Food Code mostly for Cd, Pb, Hg and As in major ten crops and many processed foods (KFDA, 2009). With implementation of Good Agricultural Practices (GAP) from 2005, the Ministry for Food, Agriculture, Forestry and Fisheries (MFAF) requires the management of harmful risk factors including toxic substances such as heavy metals, pesticides and infectious microorganisms in soil, irrigation water and fertilizers to secure crop and food safety. Laws relating to this strategy are the Soil Environment Conservation Law, the Mine Hazard Prevention Law, the Water Environment Conservation Law and the Air Environment Conservation Law, etc. However, no scientific linkage can be found among regulatory levels of heavy metals in crops, food, soils, irrigation water, fertilizers and others.

Crops can serve as a sink for metals from soil, water, air and wastes which are sources of metals. Predictions of metal bioavailability are often relied on extraction methods of metals in soils using various chemicals. The prediction of metal bioavailability is very important process for the assessment of soil pollution and the setting remedial strategy. These methods are useful under a specific condition but no method is adopted as a universal one for metal bioavailability prediction (Sauve et al., 2000). When applied to soils with a broad spectrum of metal concentrations or soil properties, they often fail to predict the metal bioavailability. In this regard, there is a lack of linkage in regulatory levels between the sources and sinks in view of crop and food safety. To find out the linkage may take a long time or be impossible. Setting the management strategy for heavy metals in soil through remedial actions might be one of the priority tasks to be undertaken for crop and food safety.

There are many state-of-the-art in-situ and ex-situ technologies developed for soil remediation which are mostly applied to heavily contaminated sites such as superfund sites in USA (Sparks, 2003). These remediation methods applicable to metal-contaminated soils are based primarily on civil-engineering decontamination techniqueswhich, for economical and practical reasons, are not applicable to arable soils. Most of these techniques do not consider redox chemistry, which is unique to paddy soils, and the techniques are usually expensive (Alvarez-Ayuso and Garcia-Sanchez, 2003). Low-cost and non-destructive alternatives that do not generate by-products should be developed for application to Cd-contaminated paddy soil.

This article reviews the management strategies for heavy metals to secure crop safety in Korea and demonstrates results of the recent case studies to retard metal translocation from soil to crops by using chemical amendments and soil layer management methods.

Regulatory Strategies for Heavy Metals in Soil and Crops

Korea Ministry for Food, Agriculture, Forestry and Fisheries (MFAFF) operates the Food Safety Information Services (FSIS) (http://www.agros.go.kr/index.jsp) to inform publics about crop safety policies. This web site serviced in Korean provides a wide range of information about crop risk, inspection, retrieval, safety management, consumer reports and consulting, etc.

The FSIS classifies the crop safety risks into chemical, biological, plant pathology and insects, animal diseases, and physical factors. Chemical risk factors include pesticide, animal pharmaceuticals, heavy metals, food additives, toxins, endocrine disruptors, and others. Biological and physical factors include pathogenic bacteria, virus, parasites, fungi and an extraneous substances. For crop safety management, systems for certification, labeling, GMO issues, and others are major services. Through various channels, this site provides consumers with valuable information about crop and food safety issues.

For a more or less special emphasis on food safety, the Korea Food and Drug Administration (KFDA) operates the on-line services (http://www.foodnara.go.kr) to provide publics with information on food labeling system, HACCP, GMO, food nutrition, functional foods, food additives, hazardous material managements, container, and other useful educational materials.

Good Agricultural Practices (GAP) refers to any collection of specific methods, which when applied to agriculture, produce results that are in harmony with the values of the proponents of those practices. GAPs are a collection of principles to apply for on-farm production and post-production processes, resulting in safe and healthy food and non-food agricultural products, while taking into account economical, social and environmental sustainability. GAPs may be applied to a wide range of farming systems and at different scales (Wikipedia, 2009).

The Ministry for Food, Agriculture, Forestry and Fisheries has adopted GAP since 2005 to manage the risk factors involved in crops and foods, such as pesticide, heavy metals and microorganisms etc. during the entire processes from production, harvest and processing to packing. Accordingly, this requires the standard regulatory criteria to control the risk factors which show a detrimental effect on production of safe crops. Thus, farmers practicing GAPs should consider the criteria for hazardous materials in soil, irrigation water, input materials and farm products. Farmers are required to check soil, irrigation water, potting soil, fertilizer and products whether they are below the safety guideline in levels of hazardous materials such as pesticides and heavy metals.

Soil Pollution Management

The Soil Environment Conservation Law (SECL) was promulgated in 1994 by MOE and was effective from 1995, in which soils of agricultural fields, forest, and urban/industrial areas have been included for application of the pollution standard. Since after, the MOE has been revised the soil environmental quality standards for additional toxic substances which may affect the crop growth and human health. Based on the continuous measurements of pollutants in soils through the monitoring networks, the soil pollution policy area will be designated and an effective control measures have been established such as risk assessment and remediation protocol etc. The cost of soil pollution policy projects is to be placed on any person responsible for such pollution. A stricter administrative measure will be taken to any to cause such pollution.

Heavy metals of As, Cd, Cu, Cr^{6+}, Hg, Pb, Ni and Zn, which are likely to cause soil contamination and restrict crop growth, were designated as the specific harmful substances under the Articles 4 and 16 of the SECL, MOE (Table 1). The standards are based on threshold values for limiting crop growth and are used as both the maximum permissible levels of such metals in agricultural soil and as the critical values for assessing the environmental impact on the soil.

Under the SECL, the nationwide monitoring network of soil quality assessment for heavy metals has been installed and operated to (1) observe the changes of metal concentration in soils, (2) use these data for soil contamination control countermeasures cooperating with regional governments, and (3) prevent soil contamination in advance. The number of monitoring locations of the network for surveying metal concentrations in soils has been increased from 780 locations in 1996 to 1,500 locations in 2005. Among them, 25.2% is the soils from agricultural areas. The analytical results have been reported annually and compiled into the Soil Groundwater Information System (SGIS: http://www.sgis.or.kr; sgisinfo@emc.or.kr). The SGIS provides archives for soil and groundwater monitoring networks results. Based on the analytical results on metal concentrations from the monitoring networks, the MOE may designate areas, corresponding to the requirements for the pollution standard criteria (Table 1), as agricultural soil pollution policy areas for the more intensive but detailed survey for metals. After the designation of a policy area, the Provincial Governor and Mayor are authorized to design the soil pollution policy projects for soil pollution prevention and removal of soil pollution, and the rationalized use of contaminated agricultural land.

Famers implementing GAPs should cultivate crops in arable soils with heavy metal contents lower than the threshold of danger level in order to be certified as the environmentally friendly or organic farm products.

Table 1. The threshold of danger level and corrective action level for soil pollution criteria in Korea.

Substances	Threshold of Danger Level (mg/kg)		Corrective Action Level (mg/kg)	
	Agricultural Area*	Factory/Industrial Area**	Agricultural Area	Factory/Industrial Area
Cd†	1.5	12	4	30
Cu†	50	200	125	500
As‡	6	20	15	50
Hg‡	4	16	10	40
Pb†	100	400	300	1,000
Cr^{6+}†	4	12	10	30
Zn¶	300	800	700	2,000
Ni¶	40	160	100	400
F	400	800	800	2,000
Organic Phosphates	10	30	-	-
PCB	-	12	-	30
CN	2	120	5	300
Phenol	4	20	10	50
BTEX	-	80	-	200
TPH	500	2,000	1,200	5,000
TCE	8	40	20	100
PCE	4	24	10	60

* Agricultural lands include soil uses for upland, paddy, orchard, pasture, forest, park, etc.
** Factory/Industry lands include soil uses for factory, road, railroad land etc.
† 0.1M HCl extraction
‡ 1.0M HCl extraction
¶ Total content extracted by aqua regia

Irrigation Water Management

The Water Environment Conservation Law designates the regulatory standards for irrigation water as shown in Table 2. Major sources of metal contamination in arable soils are derived from using acid mine drainage as an irrigation water resources in abandoned/closed mine areas (Yang et al., 2006, 2007). Thus farmers implementing GAPs should use irrigation water satisfying the regulatory standards (Table 2).

Fertilizer Management

The Fertilizer Management Law by MFAFF designates the harmful substances such as heavy metals in various fertilizers as shown in Table 3. Farmers implementing GAPs are required to use fertilizers satisfying the regulatory standards (Table 3).

Crop Safety Management

The KFDA, MFAFF and MOE had conducted the extensive nationwide monitoring to determine the heavy metal contents in 10 major crops in last 10 years. After the risk assessment of these crops to human health, the KFDA revised the food safety standards for Cd and Pb for ten crops in Dec. 21, 2006 (Table 4). These are similar to the heavy metal standards for agricultural products designated by EU and FAO/WHO Codex Alimentarius Commission (Table 5).Crops having metal levels above the standard criteria should be incinerated and discarded by farmers or provincial government.

Table 2. Regulatory standards of irrigation water

Substances	Irrigation Water Sources		
	River	Lakes	Groundwater
pH	6.0~8.5	6.0~8.5	6.0~8.5
BOD (mg/L)	8	-	-
COD (mg/L)	-	8	8
SS (mg/L)	100	15	-
DO (mg/L)	〉2	〉2	-
T-N (mg/L)	-	1.0	-
T-P (mg/L)	-	0.1	-
NO_3-N (mg/L)	-	-	20
Cl (mg/L)	-	-	250
Cd (mg/L)	0.01	0.01	0.01
As (mg/L)	0.05	0.05	0.05
Pb (mg/L)	0.1	0.1	0.1
Cr^{6+} (mg/L)	0.05	0.05	0.05
Hg (mg/L)	ND	ND	ND
CN (mg/L)	ND	ND	ND
Organic Phosphate (mg/L)	ND	ND	ND
Phenol (mg/L)	-	-	0.005
Anionic Surfactants (mg/L)	0.5	0.5	-
PCB (mg/L)	ND	ND	-
1,1,1-trichloroethane (mg/L)	-	-	0.03
Tetrachloroethlylene (mg/L)	-	-	0.01

Recently, the CODEX Alimentarius Commission adopted new standards on the maximum allowable levels of Cd in rice from 0.2 mg/kg to 0.4mg/kg. However, there have been controversies about increasing Cd standard in rice. The European Community warns that 'levels should be kept low' after they found that average dietary intake of cadmium in adults was up to 38 per cent of the Provisional Tolerable Weekly Intake (PTWI is 7 μg/kg.bw) which was set by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). The JECFA report stated that "for example, for cadmium the PTWI is 7 μg/kg body weight, which is 420 μg/ week for an average 60 kg adult and 105 μg/ week for a 15 kg child. If rice contains 0.4 mg/kg cadmium, 100 g rice alone would contribute 10 per cent of the PTWI for the adult and 40 per cent of the PTWI for the child."(http://www.foodqualitynews.com/news/).

The KFDA has been monitoring crop safety annually by analyzing heavy metal contents in major crops. For example in 2008, 450 samples of 7 crops were analyzed for metal levels and those in few samples only were exceeded the standard regulatory levels set byKFDA and CODEX (KDFA, 2009). Risk assessment based on the monitoring results indicated no risk for human health. However, metal levels in more of crop samples collected from the abandoned mine areas exceeded the crop safety criteria. Thus KFDA plans to extend the criteria for more crops and metals by carrying out the extensive monitoring for crop safety and risk assessment. This monitoring result indicates that metal levels in crop are closely related with those in contaminated soil. Thus remediation of the contaminated soil is of priority strategy to secure the crop safety.

Table 3. Standard regulatory levels of metals in fertilizers

Fertilizers	As	Cd
Ammonium Sulfate	0.05	-
Superphosphate, Double Superphosphate, Fused and Super Phosphate	0.005	0.00018
Fused Phosphate	-	0.00015
Potassium Sulfate	0.005	-
Complex Fertilizer I, II, III	0.005	0.00018
Complex Fertilizer IV	0.004	-
Hydrophonic solution	0.004	-
CDU Complex Fertilizer	0.005	0.00018

Fertilizers	Cu	Ni	Pb	As	Hg	Zn	Cd	Cr	Ti
By-Products Fertilizer (mg/kg)	500	50	150	50	2	900	5	300	-
Micronutrient Fertilizer		0.01		0.002			0.00018	0.1	0.04
Lime By-Products Fertilizer	-	0.01	-	-	-	-	-	0.1	0.04
Silicate Fertilizer	-	0.024	-	-	-	-	-	0.24	0.12
Si-P Fertilizer	-	0.024	-	-	-	-	-	0.24	0.12
Si-P-K Fertilizer	-	0.024	-	-	-	-	-	0.24	0.12
Mg Fertilizer	-	-	-	0.005	-	-	-	-	-

[Units other than by-products fertilizer is maximum % as of 1% of major ingredients]

Table 4. Maximum permissible Cd and Pb contents in 10 crops designated by KFDA.

<table>
<tr><th rowspan="3">Crops</th><th colspan="2">Korea</th><th colspan="2">CODEX</th></tr>
<tr><th>Pb</th><th>Cd</th><th>Pb</th><th>Cd</th></tr>
<tr><th colspan="4">mg/kg</th></tr>
<tr><td>Rice (Peeled)</td><td rowspan="4">0.2</td><td>0.2</td><td rowspan="4">0.2</td><td>0.4</td></tr>
<tr><td>Corn</td><td rowspan="3">0.1</td><td rowspan="3">0.1</td></tr>
<tr><td>Soybean</td></tr>
<tr><td>Red Bean</td></tr>
<tr><td>Sweet Potato</td><td rowspan="2">0.1</td><td rowspan="2">0.1</td><td rowspan="2">0.1</td><td rowspan="2">0.1</td></tr>
<tr><td>Potato</td></tr>
<tr><td>Chinese Cabbage</td><td rowspan="2">0.3</td><td rowspan="2">0.2</td><td>0.3</td><td>0.2</td></tr>
<tr><td>Spinach</td><td>0.3</td><td>0.2</td></tr>
<tr><td>Onion</td><td rowspan="2">0.1</td><td>0.05</td><td>-</td><td rowspan="2">0.1</td></tr>
<tr><td>Radish</td><td>0.1</td><td>0.1</td></tr>
</table>

Table 5. Heavy metal standards of agricultural products by EUand FAO/WHO.

<table>
<tr><th colspan="2">Heavy metals</th><th>Agricultural Products</th><th>mg/kg</th></tr>
<tr><td rowspan="6">EU</td><td>Cd</td><td>vegetables and fruits[1] (except leaf vegetables, herbs[fresh], mushrooms, stem vegetables, root vegetables, potatoes)</td><td>0.05</td></tr>
<tr><td>Cd</td><td>cereals(except wheat bran, buds, wheat, rice), stem vegetables, root vegetables, potatoes (except celeries, potatoes : apply to ML[2] of peeled potatoes)</td><td>0.1</td></tr>
<tr><td>Cd</td><td>wheat bran, buds, wheat, rice, soybeans, leaf vegetables, herbs[fresh], celery, mushroom</td><td>0.2</td></tr>
<tr><td>Pb</td><td>vegetables(except brassica, leaf vegetables, herbs[fresh], mushrooms, potatoes : apply to ML of peeled potatoes), fruits(except berries and small berries)</td><td>0.1</td></tr>
<tr><td>Pb</td><td>cereals(included buckwheats), beans, berries and small berries</td><td>0.2</td></tr>
<tr><td>Pb</td><td>brassica, leaf vegetables, cultivated mushrooms</td><td>0.3</td></tr>
<tr><td rowspan="4">FAO/ WHO</td><td>Cd</td><td>leguminous plants, beans(except dried soybeans), cereals(except buckwheats, quinoa)</td><td>0.1</td></tr>
<tr><td>Pb</td><td>tropical fruits, citrus fruits, pome fruits, stone fruits, bulbous plant, fruit vegetables, root vegetables</td><td>0.1</td></tr>
<tr><td>Pb</td><td>berries and small berries, leguminous plants, beans</td><td>0.2</td></tr>
<tr><td>Pb</td><td>Brassica vegetables, leaf vegetables</td><td>0.3</td></tr>
</table>

[1] Defined Article 1 of Directive 90/642/EEC [2] ML: Maximum Level

In Korea, soils contaminated with the threshold of danger level are managed by removing metals from soil and installing facilities to control a further pollution. Soils contaminated at above the corrective action levels are required to be remediated using physical, chemical and biological methods such as soil dressing, cover, amendments, landfill, phytoremediation etc. In the following sections, we demonstrate the experimental results from case studies about reducing metal translocation from soil to crops in view of crop safety.

Risk Assessment of Heavy Metals in the Abandoned Mine Soils

Risk analysis is comprised of risk assessment, risk management and risk communication. Risk assessment can be defined as the process of estimating both the probability that an event will occur, and the probable magnitude of its adverse effects over a specified time period (Pepper et al., 2006). There are two types of risk assessment: health-based risk and ecological risk. Since the elevated levels of heavy metals discharged from the mine wastes are found in nearby streams, agricultural soils and food crops in Korea, the risk assessment was conducted to evaluate the potential threat to human health in these areas. The risk assessment process consists of four basic steps; hazard identification, exposure assessment, dose-response assessment and risk characterization. The methods to estimate parameters in each component are shown in our previous paper (Yang et al., 2007). The major exposure pathways considered to residents were rice, groundwater and soil. The conceptual model for the human risk assessment is shown in Fig. 1(Lee et al., 2005b). The average daily dose (ADD) of the contaminant via the three identified exposure pathways was quantified for the exposure assessment to base on the hazard quotient (HQ) and hazard index (HI) formulation (Lee et al., 2005a). The HI value greater than 1 represents a toxic risk to human health through the specific exposure pathways. The higher HI value, the greater toxic risk to human health. The HI values for As and Cd in the abandoned mines were greater than 1 (Table 6). Thecancer risk for As via the pathways of rice and groundwater consumptions in the Okdong and the Hwacheon mine sites exceeded one cancer case in ten thousand (Table 7). These results demonstrated that a significant human risk could be present from the pollutions of soil, groundwater and crops in the abandoned mining sites. However, the uncertainty is inherent in every step of the risk assessment process. Thus, before we can begin to characterize the risk, we need some idea of the nature and magnitude of the uncertainty in this type of risk estimate (Pepper et al., 2006). The risk assessment suggests the priority sites and kind of metals for the bioavailability assessment and remediation. In this case study, Okdong mine area had priority to be remediated focusing on the specific treatment options for As.

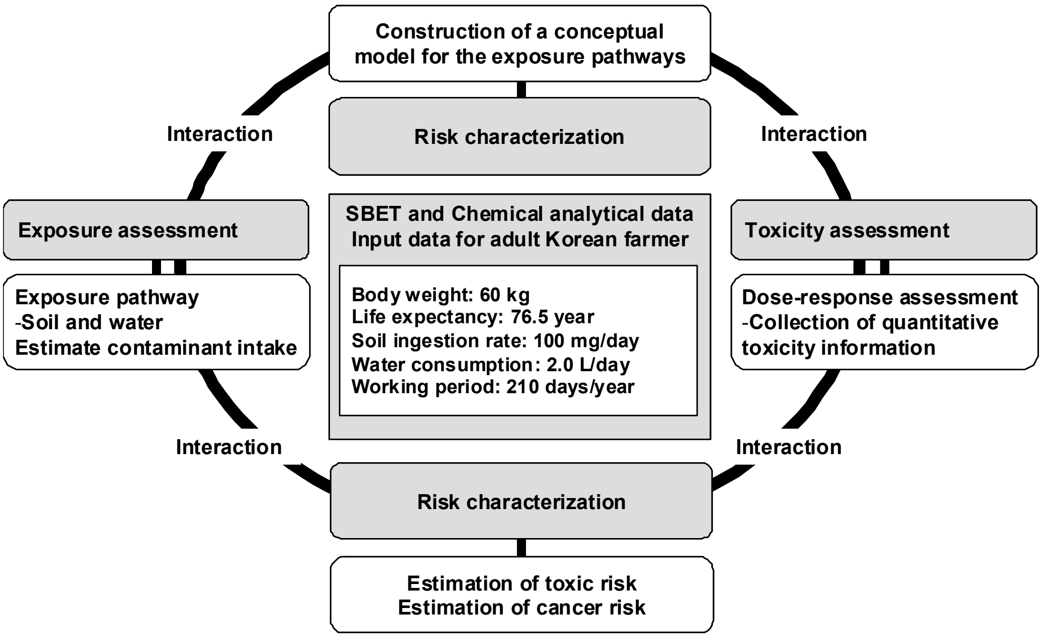


Figure 1. Risk assessment model for heavy metals in the abandoned metal mines.

Table 6. Hazard indices for As, Cd and Zn in the abandoned metal mine sites.

Mines	As	Cd	Zn
Okdong	8.88	1.11	0.44
Dokok	0.11	3.45	0.03
Hwacheon	5.38	0.97	0.57

Table 7. The cancer risk assessment of As for three exposure pathways in the three abandoned mines.

Mines	Rice grain pathway	Soil pathway	Groundwater pathway
Okdong	8.5×10^{-4}	1.3×10^{-6}	7.1×10^{-4}
Dokok	n.a.	8.5×10^{-7}	1.9×10^{-5}
Hwacheon	8.2×10^{-4}	1.2×10^{-6}	1.3×10^{-4}

Remediation Strategy of Contaminated Soils to Secure Crop Safety by Employing the Soil-Plant Barrier Concept

Introduction

Once the risk is characterized, various regulatory options should be followed to evaluate the pollution cleanup through the risk management process. The cleanup standard should follow the current regulation set by several laws. Current remediation technologies being applied to the superfund sites are impractical to be adopted in the arable soils because those methods are expensive, take a longer time and produce a secondary pollutants to be treated. Goals for remediation of arable soils should remove or immobilize contaminants from soil, recover the soil quality and function (resilience) and thus produce crops to be profitable to farmers. Thus the practical and economically and environmentally viable remedial method should be developed for arable soils. This strategy will be of importance stage to control the crop safety.

The key concepts used to describe phytoavailability are the salt effects, the plateau effect and the soil-plant barrier (Basta et al., 2005). Toxicity and bioavailability in metal spiked soil is greater than those in residual-treated soils such as biosolid and tailings. The salt effect overestimates metal bioavailability. Plant metal content plateaus at high residual loadings and the plateau is related to the residual's metal concentration and sorption capacity.

The soil-plant barrier limits translocation of many metals through the food chain, either by soil barrier or plant barrier. However, Cd is known to bypass the soil-plant barrier that can pose risks to consumers (Basta et al., 2005). The soil barrier depends in principle on any chemical reactions that can control metal bioavailability through chemical sorption, precipitation, and solubility etc. Metals in this category include Au, Ag, V and Hg etc. These metals are less likely to be bioaccumulated in upper part of plants to levels that constitute risk to consumers than metals not affected by soil barrier (Logan and Chaney, 1983 Basta et al., 2005).

The plant barrier limits translocations of metals, such as Au, Cu, Ni, Mn, Cr, As and F,from soil to crop by plant senescence from phytotoxicity. These metals result in phytotoxicity before they reach levels in the edible parts of plants often considered harmful to consumers. However, metals such as Cd, Mo, Se and Co are known to exhibit a higher risk to food chain with being less controlled by the soil-plant barrier. The degree of protection offered by the soil-plant barrier may depend on the kind of metals and plant species (Logan and Chaney, 1983).

The soil barrier options include the uses of soil ameliorants, fertilizers and irrigation control to inhibit the metal uptake by rice. Our previous works through batch and greenhouse experiments revealed that chemical ameliorants such as zero-valent iron (ZVI), compost, liquefied humus, lime or their combination lowered the phytoavailable concentrations of metals in soil solution, transformed the available fractions of metals into non-available and retarded the metal bioavailability (Yang, et al., 2007; 2008). The soil layer management reduced Cd availability from contaminated paddy soils (Yang et al., 2008).

The continuous submersion of the soil was interacted better with fertilizers than the intermittent irrigation to retard the Cd uptake by rice. The combination of NPK fertilizers with lime and compost was effective to control the Cd transfer to the rice (Yang et al., 2007). These management practices also increased the rice yield. Preliminary results showed that such conventional soil management practices could remediate the metal contaminated soils, support the yield and prevent the metal translocation to the crops.

The 24 rice cultivars were screened to compare the Cd accumulation. The Indica cultivars such as Hanyang and IR 72 rice and other cultivars such as M23 and IRI326 wereclassified as relatively high accumulating rice, even though the Cd contents were lower than the food safety guideline of the KFDA. On the other hand, the Japonica cultivars were considerably low accumulating rice for Cd. These cultivars might be screened to cultivate in the contaminated soil environment to have the metal concentration at a low enough for the safe consumption (Yang et al., 2008).

Objective of this research was to assess the efficiency of chemical ameliorants and soil layer management method, by either single treatment or combined treatment, on retardation of Cd translocation from the contaminated paddy soils to rice grain.

Materials and Methods

In the contaminated paddy field nearby the abandoned mine, where soil was contaminated by mostly Cd and Pb, soil layer management methods coupled with soil amendments were employed to evaluate the Cd availability to rice (*Oryza sativa* L.). Five treatments were installed in the paddy field: surface-subsurface layer reversing, capilary break layer using gravel, ZVI or lime layering between surface and subsurface layers and mixing the soil in surface and subsurface layers with lime. The experimental paddy field showed the spatial variability in metal distributions in situ soil profile. At one site where soil was contaminated with Cd and Pb up to 2 m depth, the contaminated soil layer to 1m depth was mixed completely with lime and rice was cultivated. At the other site, surface soil layer was contaminated with Cd and Pb up to 0.5m depth. Thus the contaminated surface layer was reversed with the non-contaminated subsurface layer. After reversing, ZVI, lime or capillary break using gravel were installed between the reversed layers. Chemical amendments used were lime, ZVI and slag, etc. In each treatment, soil solution sampler and ion exchage resin capsules were installed at different depths to monitor the changes of available metal concentrations. Amberlite IRN-150 and Chelex 100 resin were made into spherical form (resin capsules) using the polyester cloths (Yang et al., 1991; Yang and Skogely, 1992). At diferent growth stages of rice after transplanting, samples of soil, water and resin were taken and analyzed for metals. Rice yield andCd concentrations in rice and soils were analyzed after harvest. The efficiency of these methods to retard Cd and Pb uptake by rice (*Oryza sativa* L.) was evaluated based on 0.1M HCl extractability, fractionation, soil solution, ion exchange resin extractability, growth and yield parameters of rice and metal concentrations in rice by comparing concentrations before and after treatments.

Results

The soil layer management methods were effective in inhibiting Cd and Pb uptakes by rice (Table 8). The content of Cd in rice was 0.95 mg/kg in the control which exceeded both Korean standard (0.2mg/kg) and CODEX guideline (0.4 mg/kg). The Pb contents in rice of the control were 2.94 mg/kg and those in the treatments were higher than 1.0 mg/kg which are exceeding the maximum permissible Pb contents in rice designated by KFDA (0.2mg/kg). Thus a precaution for Pb level in rice grown in the contaminated paddy field needs to be taken.

Efficiencies of the soil layer management methods in retardation of metal uptake were about 76% for Cd and 60% for Pb. Layering the ZVI and lime between the non-contaminated surface layer and contaminated subsurface layer was effective methods but needs a further field work. Thus, either reversing the surface layer with subsurface layer or immobilization of metals with layer mixing with lime might be the practical option for the in-situ application.

Table 8. Effects of soil layer management methods on metal uptake by rice.

Treatment	Metals in Rice (mg/kg)	
	Cd	Pb
Soil layer reversing	0.24(74.7%)[‡]	1.26(57.1%)
ZVI layer	0.21(77.9%)	1.16(60.5%)
Lime layer	0.22(76.8%)	1.16(60.5%)
Capillary break layer	0.23(75.8%)	1.11(62.2%)
Layer mixing with lime	0.25(73.7%)	1.28(56.5%)
Control	0.95	2.94

‡ efficiency of treatments as compared to the control.

Table 9 showsthe changes of pH and concentrations of Cd and Pb in soil as affected by soil layer management methods at transplanting and harvest periods. Rice yield was increased with soil layer treatments as compared to the control. pH at the ZVI layering and lime mixing treatments were higher than that of the control. In these treatments, concentrations of Cd and Pb in soil were effectively decreased at harvesting period. However, lime layer and capillary break treatments, Cd concentrations were increased at harvest period.

Table 9. Changes of pH and concentrations of Cd and Pb in soil, and rice yields as affected by soil layer management methods at different rice growing periods.

Treatments	pH		Cd		Pb		Rice Yield
	Transplanting	Harvest	Transplanting	Harvest	Transplanting	Harvest	
			mg/kg		mg/kg		MT/ha
Control	6.82	6.92	4.03	4.67	300	75	7.0
Layer reversing	6.47	6.74	5.22	5.21	670	513	13.4
ZVI layer	8.43	8.55	3.65	0.56	190	1.00	12.6
Lime layer	6.53	7.00	1.35	6.45	168	334	12.9
Capillary break	6.65	6.72	4.37	6.13	510	398	15.4
Lime mixing	8.29	8.28	6.70	4.84	517	423	13.2

Figure 2shows the effects of treatments on the residual concentrations of Cd in paddy soil. Treatment reduced the extractable Cd as compared to the control. Among treatments, capillary break, ZVI layer and lime layer were more effective than reversing and mix treatments.

Figure 3 shows the efficiencies of chemical ameliorants on the changes of 0.1M HCl extractable Cd at different growth periods of rice as compared to the control. Such chemical amendments slightly reduced the Cd extractability and their efficiencies were varied with treatment concentrations and time. This reduction might be related with adsorption of Cd onto chemicals or immobilization of Cd at increased pH condition by added lime and slag.

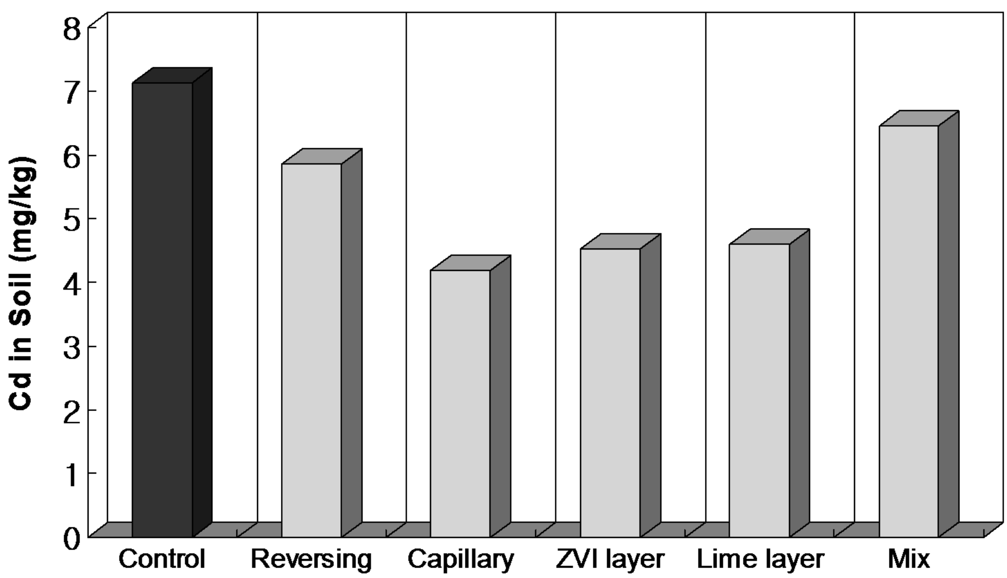


Figure 2. Effects of treatments on the residual concentrations of Cd in paddy soil.

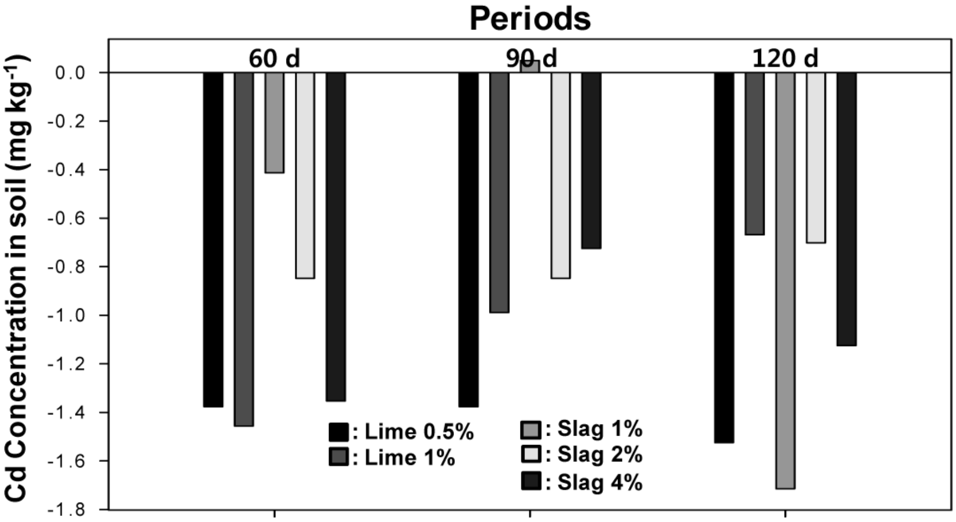


Figure 3. Effects of chemical ameliorants on the changes of 0.1M HCl extractable Cd at different growth periods of rice.

Figure 4shows the effects of chemical soil amendments on changes of pH and Cd concentration in soil solution in June and September. Chemical ameliorants such as lime, slag and compost increased pH of soil solution as compared to the control and this trend was more evident as treatment time was elapsed. The high pH for example greater than 5.6 is supposed to immobilized or precipitated heavy metals by forming hydroxides or oxides compounds (Sparks, 2003). Concentrations of Cd in soil solution were sharply decreasedas compared to the control with chemical amendment treatments. The decreases in Cd soil solution were more evident in Sept. than June. This result might be related to the decreases in available Cd and translocation into rice.

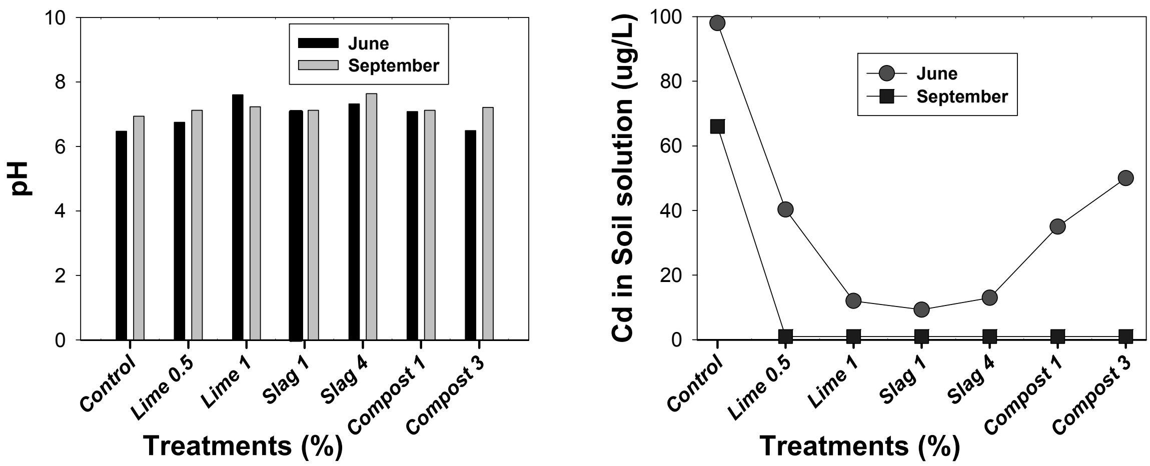


Figure 4. Effects of chemical soil amendments on changes of pH and Cd concentration in soil solution.

Figure 5 shows the effects of chemical ameliorants and soil layer management methods on the changes of Cd fractions in surface and subsurface soils. Fractions 1 and 2 are generally considered as available fractions and fractions 4 and 5 as non-available fractions. Treatments tended to decrease the available factions and on the other hand increase the non-available fractions. These results are coincided with those from batch and greenhouse pot experiments (Yang et al., 2007).

Figure 6 shows the Cd concentration extracted by ion exchange resin capsules. Phytoavailability Soil Test (PST) uses the Amberlite IRN-150 which is 1:1 mixture of H^+ and OH^-saturated resins. Chelex 100 resin is heavy metal selective resin. Thus metals extracted by these resin capsules based on the interfacial diffusion kinetics from soil solution are considered as available metal fractions (Yang et al., 1991; Yang and Skogley, 1992). As shown in Fig. 6, resin adsorption quantity (RAQ) extracted by the spherical resin capsules were decreased by lime and slag treatments with a higher decrement as treatment dose increased. Also soil layer management methods decreased in general the resin adsorption quantity. These results demonstrate that chemical amendments and soil layer management method are useful tools to decrease the Cd bioavailability and thus translocation into rice.

Discussion

There is growing concernin Korea over the elevated levels of metals in crops and foods. Heavy metals are classified as the chemical harmful risks for crop and food safety. With implementation of GAP, crop safety is controlled by many regulatory options in soil, irrigation water and fertilizers. However there is lack of linkage between regulatory criteria for metals in crops and those in soil, water and fertilizers. Metal concentrations in crops are largely dependent upon metals in soil. Metal translocation from soil to crop especially to above ground portion is controlled by factors governing the phytoavailability of metals which are in turn affected by soil, plant and metal factors (Yang et al., 2007; Basta et al., 2005; Sparks, 2003). Therefore any attempt to retard the metal uptake by crops may be the best protocol to secure crop and food safety. After metals being taken up by crops, there seems to be no virtual remedy to secure crop safety. However, a technology to retard the metal translocation from soil to crop should be environmentally and economically viable considering arable lands. Our previous works reveal that soil-plant barrier concepts (Basta et al., 2005; Logan and Chaney, 1983) are promising tool to reduce the metal bioavailability using soil and plant factors (Yang et al., 2007, 2008).

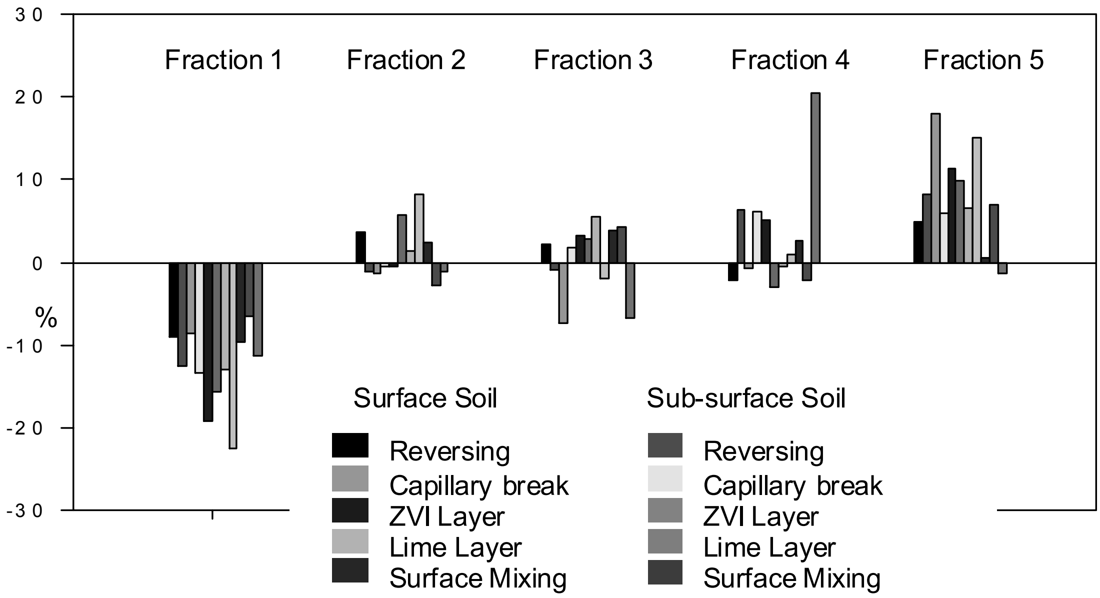
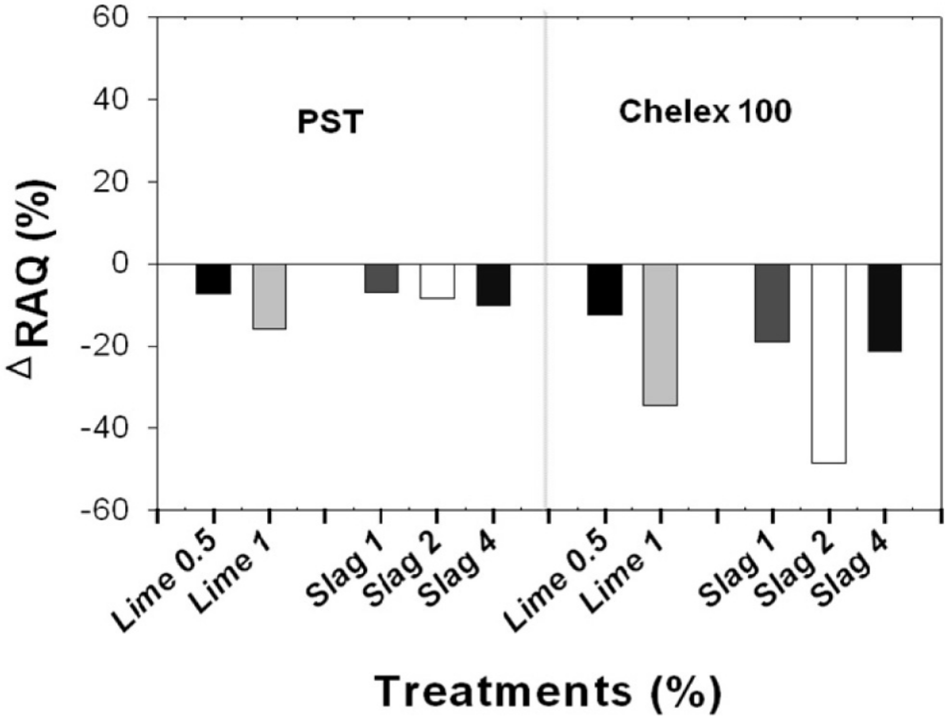


Figure 5. Effects of chemical amendments and soil layer management methods on Cd fractions in surface and subsurface soils.

Under the field conditions, profiles for heavy metal contaminations are site-specific showing a lot of spatial variability. Thus a single protocol to inhibit the metal availability is nearly impossible. Figure 7 shows the pattern for metal distribution in the contaminated soil profiles. These pitfalls can be negated by using the combined treatments of chemical ameliorants and soil layer management methods.

Chemical ameliorants such as lime, ZVI, compost and slag are easily accessible since they are mostly commercially available or by-products. Those can increase pH of the soil solution and thus immobilize metals into insoluble compounds which are unavailable for crop uptake (Yang et al., 2007, 2008). The longevity of chemical amendments may be varied with amounts applied soil conditions but it seems to be effective for a longer period. This method is relatively cheaper to practice as compared to the current remediation technologies (Sparks, 2003).



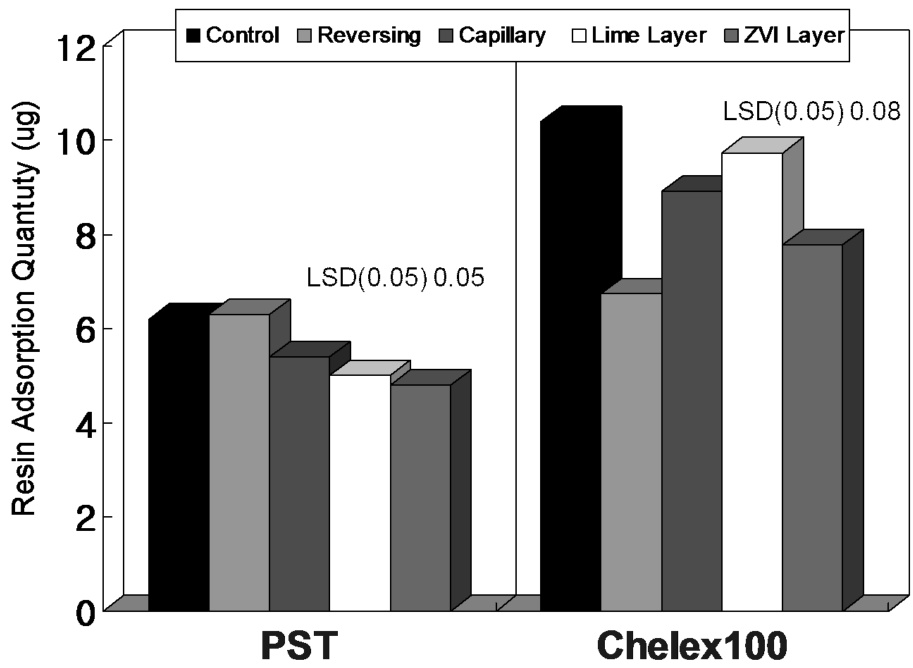


Figure 6. Effects of chemical amendments (above) and soil layer management methods on Cd extraction by two different ion exchange resin capsules.

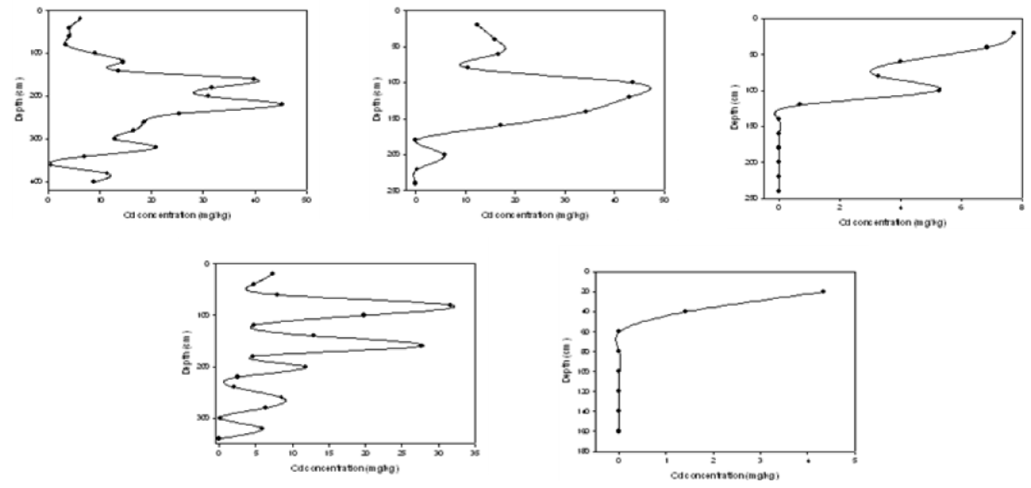


Figure 7. Heavy metal distributions in the contaminated soil profile near the abandoned mines.

Since heavy metals in soil are relatively immobile, a complete removal of metals from soil might be impossible for economical and practical reasons. Most of metals in surface soils can be taken up by plant roots. Metal concentrations in surface soils can be diluted by covering or dressing with unpolluted soils. Covering or dressing soils should have the proper physical and chemical properties to reclaim the contaminated soils. In case surface soil is contaminated and subsurface soil is clean, then these layers can be reversed to secure a low concentration of metal in surface soils. Deep plowing may dilute the metal concentration in surface soil by mixing with unpolluted subsurface soil. Installment of capillary break between surface and subsurface layers can inhibit the metal transport by base flow from the contaminated subsurface soils to the rhizosphere. The longevity of soil layer management method might however be a pitfall for metal stabilization in soil because metals can be translocated into crop over a long term. Therefore to secure crop safety by stabilizing or dilution requires the combination of chemical ameliorants and physical layer management method. Based on our previous experiences, we suggest the following flowchart to remediate the contaminated arable soils (Figure 8).

Combination of chemical soil amendments and layer management methods are promising to retard the metal bioavailability and thus to secure crop safety for heavy metals. This protocol seems to be cheap, easy to practice and practical in the agricultural fields. Remediation of arable land should meet the goals such as removal of metal, immobilization of metals, recovery of soil quality and functions, and sustaining the yield and profits for farmers. In this regard, the scheme shown in Fig. 8 might be a potent tool to secure crop safety grown in contaminated lands. However, a long term monitoring work should be followed to verify the efficiency of this protocol.

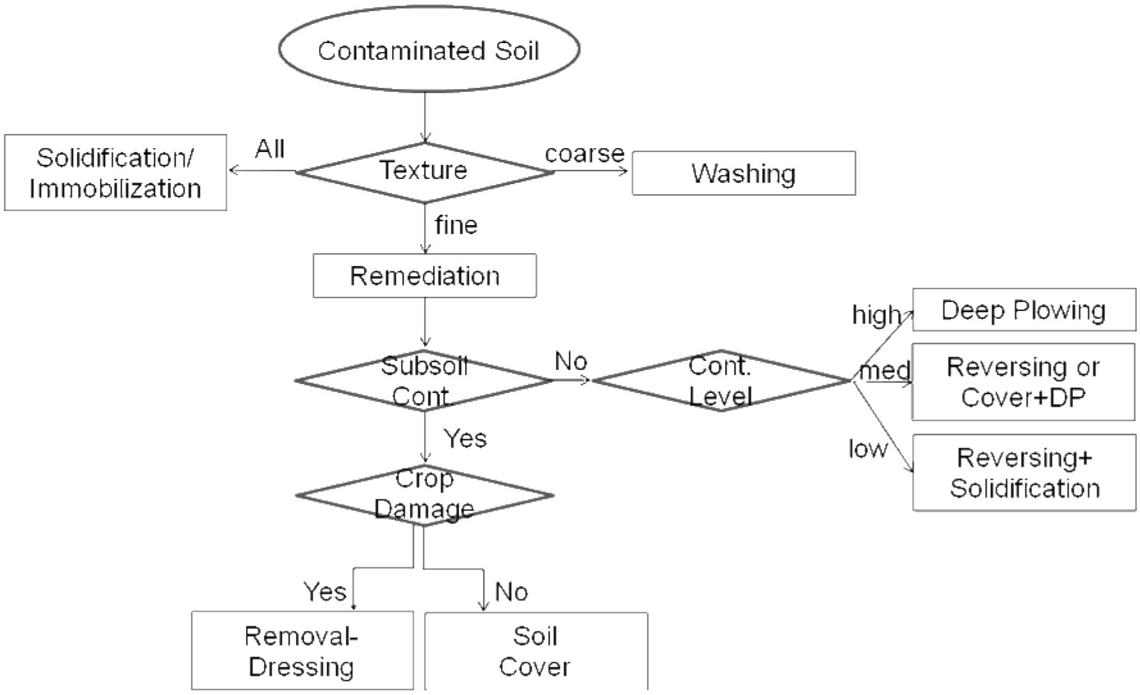


Figure 8. Flowchart of the combined chemical amendments and layer management methods to secure crop safety against the harmful heavy metals in arable soils.

Conclusion

Paddy soil has been contaminated mostly by the abandoned mining wastes such as acid mine drainage and tailings in Korea. In certain locations nearby the abandoned mines, concentrations of Cd and Pb in rice exceed the safety guideline which is 0.2 mg/kg. Risk assessment for human health revealed that rice and groundwater consumptions were the major exposure pathways to human showing a potential health threat. The practical protocol for remediation of the contaminated arablesoil is needed to develop in view points of food safety and soil quality conservation. Current remediation technologies based on the civil-engineering or biotechnology principles are not applicable to paddy fields considering the inherent chemistry of paddy soil, besides the economical and environmental pitfalls. Greenhouse experiments showed that chemical amendments such as lime, ZVI or compost effectively immobilized metals in soil and retarded the metal translocation to rice (*Oryza sativa* L.). These amendments also converted the available fractions of Cd in soil into the non-available fractions. Layer management methods in the metal contaminated fields, coupled with chemical amendments practices, decreased the uptake of Cd by 76% and Pb by 60%. Irrigation control of the continuous submersion rather than intermittent irrigation might help reduce the metal translocation to rice. Combination of chemical fertilizer with chemical amendments such as compost and lime reduced the Cd uptake by rice. In the metal contaminated paddy soils, the screening the pollution safe cultivar might be a potential approach to reduce the human health risk due to metal intake through the rice consumption. Results demonstrated that combinations of chemical amendments with soil layer management practices in the metal-contaminated paddy soils were considered to be the practical option for the *in-situ* remediation to secure crop safety.

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