MARCO-FFTC Joint International Seminar on Management and Remediation Technologies of Rural Soils Contaminated by Heavy Metals and Radioactive Materials

Taiwan Agricultural Research Institute (TARI), Council of Agriculture, Taiwan

Sep 23~24, 2014
Proceedings of
MARCO-FFTC Joint International Seminar on
Management and Remediation Technologies of
Rural Soils Contaminated by Heavy Metals and
Radioactive Materials

Taiwan Agricultural Research Institute (TARI), Council of Agriculture
Taichung, Taiwan

Sep 22-26, 2014
Background and rational

In the last two decades, there has been a successive aggravation and deterioration in soil quality because of rapid urbanization, industrialization, intensive farming, and so forth, while a large amount of various pollutants were piled up in the soil and water systems in Asian countries. This phenomenon, in turn, caused further deterioration in environmental quality and posed a serious risk to human health.

Codex and WHO has recently proposed a new standard of some hazardous chemical concentrations in major agricultural products such as rice grain, wheat and vegetables, and some Asian countries have revised the critical concentrations (or regulation) of heavy metals or pollutants in the soils and crops in Asian countries in last five years, including Taiwan, Japan, and Korea. With rice being an important staple crop in many Asian countries, it becomes a matter of urgency to reduce hazardous chemical concentrations such as Cd, As, Pb, Cu, and Zn, especially in paddy soil and rice grains of Cd, Pb and As.

Taiwan EPA will make a revision on the regulation of heavy metals in rural soils in the end of 2013. This revision of regulation of heavy metals in rural soils are regarded as the more consideration and evaluation on the health risk assessment of heavy metals in soils and crops, including As, Cd, Pb, Cu, Zn, Cr (VI), Cr (III), Ni, and Hg.

Recently, it was reported that 25% of wells in Bangladesh are polluted by arsenic and that more than 30 million people are left with no other options but to drink As-polluted water from the groundwater. Since then, intensive surveys have been conducted in various Asian countries where people are fully dependent on the underground water for drinking and also for irrigation of rice production. Unfortunately, arsenic in soil and groundwater pollution is a serious problem not only in Bangladesh, but also in many other Asian countries, such as China, Vietnam, Cambodia, Myanmar, Nepal, India, Thailand, Pakistan, and also in southern Taiwan in last decade. It has also been reported that the mechanism of groundwater pollution by arsenic is closely associated with geology and agricultural practices, particularly irrigation water in southern Taiwan.

There was a big earthquake off the eastern coast of Japan in 2011. The resulting tsunami devastated Fukushima Dai-ichi nuclear power plant, resulting in one of the most serious accidents in the history of nuclear industry. A large amount of radionuclide fallout contaminated the environment which affected the soil and agricultural products. More than 8,000 ha of farmland in Fukushima prefecture were suspended to be cultivated.

The amount of radioactive cesium (134 Cs and 137 Cs) transferred from soil to crops is affected not only by its concentration in soil but also by soil type and soil management practices such as fertilizer application and tillage. The soil contamination by radioactive cesium, particularly 137 Cs, which possesses a decaying half-life of 30 years causes serious problem over the long-time. Farming in highly contaminated soils requires intensive remediation practices. Application of potassium fertilizers and adsorbents are effective to minimize the uptake of radioactive cesium by plants.

This international seminar aims to identify and develop reliable, economically feasible and effective remediation technologies for the polluted soil and groundwater by radioactive-Cs and non-radioactive relevant chemicals, in particular heavy metals of As, Cd, Pb, and As.
Objectives
1. To understand the status of rural soils contaminated by heavy metals (or radioactive materials) and management strategies of food safety of crops grown in the contaminated sites in each country.
2. To study and review the relationships between heavy metals (or radioactive materials) in the crops and their contents in the contaminated soils, and also to develop the technology to reduce the uptake of pollutants by crops and how to develop the regulations of pollutants in the soils and crops;
3. To collect the biological, chemical and physical soil management and remediation technologies for cost-effective remediation on targeted heavy metals (or radioactive materials) of the contaminated rural soils; and
4. To share and exchange relevant information on cost-effective remediation technologies for reducing the target heavy metals (or radioactive materials) in the contaminated sites.

Expected outputs
1. To better understanding of the current status of hazardous chemical pollution in arable soil and groundwater system in Asian countries;
2. To identify the various potential soil management and remediation practices for the Asian rural soils contaminated by heavy metals or radioactive materials; and
3. To develop an integrated remediation technology or soil management practice to reduce the heavy metals or radioactive materials in the Asian polluted rural soils and groundwater.

Language: English

Venue
This seminar will be held at Taiwan Agricultural Research Institute (TARI), Council of Agriculture, Taichung, Taiwan. http://www.tari.gov.tw

Accommodation
(1) Hotel National
No.57, Guanqian Road, West Dist., Taichung, Taiwan
Tel: +886- 4-2321-3111; Fax: +886-4-2321-3124
http://www.hotel-national.com.tw
and
(2) Howard Civil Service International House
No.30, Sec. 3, Shin-Sheng South Road, Taipei, Taiwan
Tel : +886-2-7712-2323; Fax: +886-2-7712-2333
http://intl-house.howard-hotels.com
Program

MARCO-FFTC Joint International Seminar on Management and Remediation Technologies of Rural Soils Contaminated by Heavy Metals and Radioactive Materials
(受重金屬與放射性物質污染之農田土壤管理與整治技術國際會議)

Taiwan Agricultural Research Institute (TARI), Council of Agriculture, Taiwan
Sep 22-26, 2014

September 22 (Monday)
All invited speakers will arrive in Taipei (Taoyuan) international airport and will be driven to Taichung city using FFTC arranged Shuttle Services.

September 23 (Tuesday)
08:30- 09:00 Registration
Master of Ceremonies: Mr. Ronald MANGUBAT (FFTC)

Opening Ceremony
09:00- 09:20

Opening Address

Mr. Wen-Deh CHEN
Vice Minister
Council of Agriculture, Executive Yuan, R.O.C.(Taiwan)

Dr. Yu-Tsai HUANG
Director
Food and Fertilizer Technology Center (FFTC) for the Asian and Pacific Region

Welcome Remarks

Dr. Tomohito ARAO
Principal Research Coordinator
National Institute for Agro-Environmental Sciences, Japan

Dr. Hung-Teh TSAI
Executive Secretary
Soil and Groundwater Remediation Fund Management Board, EPA, Taiwan

Dr. Junne-Jih CHEN
Director General
Taiwan Agricultural Research Institute (TARI), Council of Agriculture, Taiwan

Session 1 Keynote Speech
Moderator: Dr. Zueng-Sang CHEN (Taiwan)
09:30-10:20  Cd and As contamination of Agricultural Products and Countermeasures in Japan  
Dr. Tomohito ARAO  
Principal Research Coordinator  
National Institute for Agro-Environmental Sciences, Japan

10:20-10:30  General Discussion

10:30-10:40  Group Photo

10:40-11:00  Coffee/Tea Break

Session 2  The Relationships Between Heavy Metals in Crops and their Contents in Contaminated Soils  
Moderator: Prof. Dr. Dar-Yuan LEE (Taiwan)

11:00-11:30  The Relationships of Cd Concentration in Arable Soil and Different Rice Varieties and the Food Safety Evaluation of Different Brown Rice Varieties in Taiwan  
Mr. Horng-Yu GUO  
Division Chief, Division of Agricultural Chemistry  
Taiwan Agricultural Research Institute (TARI), Taiwan

11:30-12:00  The Relationships of Heavy Metals Concentration in Arable Soil, Rice Varieties and Vegetables and the Food Safety Evaluation of Agricultural Crop Production in Thailand  
Dr. Orathai SUKREYYAPONGSE  
Director, Office of Science for Land Development  
Land Development Department, Thailand

12:00-13:30  Lunch

13:30-14:00  The Relationships between Cd Concentration in Arable Soils and Different Vegetables and the Evaluation of Food Safety of Vegetables in Taiwan  
Ms. Yu-Wen LIN  
Assistant Researcher, Agricultural Information Service Lab., Division of Agricultural Chemistry, Taiwan Agricultural Research Institute (TARI), Taiwan

14:00-14:20  General Discussion

Session 3  Soil Remediation Technologies for Heavy Metals Contaminated Soils  
Moderator: Dr. Tomohito ARAO (Japan)

14:20-14:50  Advanced Physico-chemical Method to Restore Agricultural Soils Contaminated with Cd and Radioactive Cesium  
Dr. Tomoyuki MAKINO  
Senior Reseracher, Soil Environmental Division  
National Institute for Agro-Environmental Sciences, Japan

14:50-15:20  Smart Biochar Technology for Remediation of Toxic Metals in Soils  
Prof. Yong Sik OK  
Director, Korea Biochar Research Center, Department of Biological Environment, Kangwon National University, Korea

15:20-15:40  General Discussion

15:40-16:00  Coffee/Tea Break
Session 4  
Soil Remediation Technologies for Radioactive Materials-Contaminated Soils  
**Moderator:** Dr. Tomoyuki MAKINO (Japan)

16:00-16:30  
**Monitoring of Radio-cesium Contamination in Farmland Soil in Eastern Japan**  
Dr. Kazunori KOHYAMA  
Senior Researcher, Natural Resources Inventory Center  
National Institute for Agro-Environmental Sciences, Japan

16:30-17:00  
**Mitigation of Radioactive Contamination from Farmland Environment and Agricultural Products**  
Dr. Takuro SHINANO  
Tohoku Agricultural Research Center (TARC)  
National Agriculture and Food Research Organization (NARO), Japan

17:00-17:20  
**General Discussion**

18:30 - 20:30 Welcome Dinner  
B1, VIP Room (貴賓廳), Hotel National  
Hosted by **Dr. Junne-Jih Chen**, Director General, TARI

**September 24 (Wednesday)**

08:30- 09:00  
**Registration**

09:00-09:30  
**Development of Low-Cd Rice by Mutation with Ion-beam**  
Dr. Satoru ISHIKAWA  
Senior Researcher, Soil Environmental Division  
National Institute for Agro-Environmental Sciences, Japan

09:30-10:00  
**Effect of Iron Plaque and Rice Genotypes on As Accumulation in Rice Plants Grown in As-contaminated Paddy Soils**  
Prof. Dr. Dar-Yuan LEE  
Distinguished Professor of Soil Chemistry, Department of Agricultural Chemistry, National Taiwan University, Taipei, Taiwan

10:00-10:20  
Coffee/Tea Break

10:20-10:50  
**Comparison of Various Single Chemical Extraction Methods for Predicting the Bioavailability of Arsenic in Paddy Soils**  
Dr. Won-Il KIM  
Research Scientist, Chemical Safety Division, National Academy of Agricultural Science (NAAS), Rural Development Administration (RDA), Korea

10:50-11:20  
**New Regulation Development for Soil Remediation of Heavy Metal Contaminated Sites and Health Risk-based Approaches in Taiwan**  
Prof. Dr. Zueng-Sang CHEN  
Distinguished Professor of Pedology and Soil Environmental Quality, Department of Agricultural Chemistry, National Taiwan University, Taiwan
11:20-11:40 General Discussion
11:40-12:40 Lunch
12:40-13:40 Taiwan Soil Museum, TARI

Session 6
The Status of Rural Soils Contaminated by Heavy Metals and Management Strategies
Moderator: Dr. Satoru ISHIKAWA (Japan)
13:40-14:10 In-situ Immobilization of Selected Heavy Metals in Soils Using Agricultural Wastes and Industrial By-products
Prof. Dr. Che Fauziah ISHAK
Deputy Dean, Faculty of Agriculture
Department of Land, University of Putra Malaysia (UPM), Malaysia
14:10-14:40 Heavy Metal Contamination and Remediation Practices of Soils in the Philippines
Dr. Rodolfo O. ILAO
Supervising Science Research Specialist, Philippine Council for Agriculture, Aquatic and Natural Resources Research and Development (PCAARRD), Philippines
14:40-15:10 Level of Heavy Metals in Agricultural Soil and Water After Mount Sinabung Eruption in North Sumatera, Indonesia
Dr. Asep NUGRAHA
Agrochemical Residue Laboratory, Indonesian Agricultural Environment Research Institute Indonesia
15:10-15:30 Coffee/Tea Break

Session 7
The Status of Rural Soils Contaminated by Heavy Metals and Management Strategies
Moderator: Dr. Rodolfo O. ILAO (Philippines)
15:30-16:00 Heavy Metals in Agricultural Soil and Using Plants to Clean Up Contaminated Soils (Phytoremediation) in Vietnam
Dr. Tran Minh TIEN
Head, Soil Genesis and Classification Research Department
Soils and Fertilizers Research Institute (SFRI), Vietnam
16:00-16:30 Arsenic and Other Heavy Metal Status in Soils and Crops in Bangladesh
Dr. Baktear HOSSAIN
Principal Scientific Officer, Soils Unit, Natural Resources Management Division
Bangladesh Agricultural Research Council, Bangladesh
16:30-17:00 Land Use and Land Degradation Situation in Cambodia, and Possible Solutions
Dr. Sovuthy PHEAV
Director, Department of Agricultural Land Resources Management, Ministry of Agriculture, Forestry and Fisheries, Cambodia
17:00-17:20 General Discussion
Session 8     General Discussion of Seminar and Closing Ceremony
17:20-17:50     General Discussion of Seminar
Chair: Dr. Tomohito ARAO
Dr. Zueng-Sang Chen, Prof. Dr. Yong Sik OK
Dr. Tran Minh TIEN, Dr. Orathai SUKREEYAPONGSE

17:50-18:00     Closing Ceremony
18:30-20:30     Farewell Dinner
B2, Chung Kang-Wen Hsin Room (中港-文心廳), Evergreen Laurel Hotel
Hosted by Dr. Yu-Tsai Huang, Director, FFTC

September 25 (Thursday)

Field Trip

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<td>Bus to Houli, Taichung (45mins)</td>
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<td>09:15 – 10:30</td>
<td>Visiting the experiment field of 120 rice varieties uptake cadmium assessment at Houli (后里) (1.5hrs)</td>
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<td>10:30 – 12:00</td>
<td>Bus to Sun Moon Lake – Shueishe (水社) (1hr30mins)</td>
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<tr>
<td>12:00 – 13:30</td>
<td>Lunch at Hotel Del Lago (1.5hrs)</td>
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<td>日月潭大淶閣 南投縣魚池鄉中山路 101 號 049-2856602</td>
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<tr>
<td>13:30 – 14:30</td>
<td>Boat Cruise in Sun Moon Lake (水社-玄光寺-水社) (1hr)</td>
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<tr>
<td>14:30 – 14:40</td>
<td>Bus to Yuch’ih Substation, Tea Research and Extension Station (TRES)</td>
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<tr>
<td>14:40 – 16:00</td>
<td>Visit Yuch’ih Substation, Tea Research and Extension Station (TRES) (1hr20mins)</td>
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<td></td>
<td>南投縣魚池鄉水社村中山路 270 巷 13 號 049-2855106</td>
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<tr>
<td>16:00 – 18:00</td>
<td>Bus to Miao-Li (2hrs)</td>
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<td>18:00 – 19:30</td>
<td>Dinner at Miao-Li (1.5hrs)</td>
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<tr>
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<td>紅棗食府 公館鄉福基村 3 鄰 45 號 03 722 4688 ($3000*2T)</td>
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<td>19:30 – 21:00</td>
<td>Bus to Taipei (1.5hrs)</td>
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Stay at Howard International House
台北市新生南路三段 30 號

September 26 (Friday)

Departure of Overseas Participants
List of Participants

Opening Ceremony:

Opening Remarks

Mr. Wen-Deh CHEN (陳文德)
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Council of Agriculture, Executive Yuan, R.O.C.(Taiwan)
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Dr. Yu-Tsai HUANG (黃有才)
Director
Food and Fertilizer Technology Center (FFTC) for the Asian and Pacific Region
Email: ythuang10@gmail.com

Welcome Remarks

Dr. Tomohito ARAO (荒尾 知人)
Principal Research Coordinator
National Institute for Agro-Environmental Sciences, Japan
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Dr. Hung-Teh TSAI (蔡鴻德)
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Dr. Junne-Jih CHEN (陳駿季)
Director General
Taiwan Agricultural Research Institute (TARI), Council of Agriculture, Taiwan
Email: jjchen@tari.gov.tw

Opening Remarks

Session 1: Keynote Speech

1-1 Japan
Dr. Tomohito ARAO (荒尾 知人)
Principal Research Coordinator
National Institute for Agro-Environmental Sciences, Japan
Email: arao@affrc.go.jp

Session 2: The Relationships Between Heavy Metals in Crops and their Contents in Contaminated Soils

2-1 Taiwan
Mr. Horng-Yu GUO (郭鴻裕)
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Division of Agricultural Chemistry, Taiwan Agricultural Research Institute (TARI), Taiwan
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2-2 Thailand  Dr. Orathai SUKREEYAPONGSE  
Director  
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2-3 Taiwan  Ms. Yu-Wen LIN (林毓雯)  
Assistant Researcher  
Agricultural Information Service Lab. Division of Agricultural Chemistry, Taiwan Agricultural Research Institute (TARI), Taiwan  
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Session 3: Soil Remediation Technologies for Heavy Metals Contaminated Soils  

3-1 Japan  Dr. Tomoyuki MAKINO (牧野知之)  
Senior Researcher  
Soil Environmental Division, National Institute for Agro-Environmental Sciences (NIAES), Japan  
Email: t_makino@affrc.go.jp  

3-1 Korea  Prof. Yong Sik OK  
Director  
Korea Biochar Research Center, Department of Biological Environment, Kangwon National University, Korea  
Email: soilok@kangwon.ac.kr  

Session 4: Soil Remediation Technologies for Radioactive Materials-Contaminated Soils  

4-1 Japan  Dr. Kazunori KOHYAMA (神山和則)  
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Natural Resources Inventory Center, National Institute for Agro-Environmental Sciences, Japan  
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4-2 Japan  Dr. Takuro SHINANO (信濃卓郎)  
Tohoku Agricultural Research Center (TARC)  
National Agriculture and Food Research Organization (NARO), Japan  
Email: shinano@affrc.go.jp  

Session 5: New Developed Strategies and Remediation Technologies for Food Safety of Crops Grown in Contaminated Soils  

5-1 Japan  Dr. Satoru ISHIKAWA (石川覚)  
Senior Researcher  
Soil Environmental Division, National Institute for Agro-Environmental Sciences (NIAES), Japan  
Email: isatoru@affrc.go.jp  

5-2 Taiwan  Prof. Dr. Dar-Yuan LEE (李達源)  
Distinguished Professor of Soil Chemistry  
Department of Agricultural Chemistry, National Taiwan University, Taiwan  
Email: DYLEE@ntu.edu.tw
5-3 Korea  Dr. Won-Il KIM (金源益)
Research Scientist
Chemical Safety Division, National Academy of Agricultural Science (NAAS), Rural Development Administration (RDA), Korea
Email: wikim721@korea.kr

5-4 Taiwan  Prof. Dr. Zueng-Sang CHEN (陳尊賢)
Distinguished Professor of Pedology and Soil Environmental Quality
Department of Agricultural Chemistry, National Taiwan University, Taiwan
Email: soilchen@ntu.edu.tw

Session 6:  The Status of Rural Soils Contaminated by Heavy Metals and Management Strategies

6-1 Malaysia  Prof. Dr. Che Fauziah ISHAK
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6-2 Philippines  Dr. Rodolfo O. ILAO
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6-3 Indonesia  Dr. Asep NUGRAHA
Agrochemical Residue Laboratory, Indonesian Agricultural Environment Research Institute, Indonesia
Email: asena@indo.net.id

Session 7:  The Status of Rural Soils Contaminated by Heavy Metals and Management Strategies

7-1 Vietnam  Dr. Tran Minh TIEN
Head
Soil Genesis and Classification Research Department, Soils and Fertilizers Research Institute (SFRI), Vietnam
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7-2 Bangladesh  Dr. Baktear HOSSAIN
Principal Scientific Officer, Soils Unit
Natural Resources Management Division, Bangladesh Agricultural Research Council, Bangladesh
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7-3 Cambodia  Dr. Sovuthy PHEAV
Director
Department of Agricultural Land Resources Management, Ministry of
Observer:

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Mr. Chun-Lang CHEN (陳俊郎)  
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## The relationships of Cd concentration in arable soil and different rice varieties and the food safety evaluation of different brown rice varieties in Taiwan

Horng-Yu Guo*, P.F.A.M. Römken

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## The relationships of heavy metals concentration in arable soil, rice varieties and vegetables and the food safety evaluation of agricultural crop production in Thailand

Orathai Sukreeyapongse*, Jutharat Khumnungkit, Lamai Srisawat, Onanong Chomsiri, Napassorn Notesiri

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## The relationships between Cd content in arable soils and different vegetables and the evaluation of food safety of vegetables in Taiwan

Yu-Wen Lin*, Tsang-Sen Liu, Horng-Yuh Guo, Chih-Min Chiang

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## Advanced physico-chemical method to restore agricultural soils contaminated with Cd and radioactive cesium

Tomoyuki Makino*, Hiroyuki Takano, Takashi Kamiya, Yuji Mejima, Ikuko Akahane, Naoki Sekiya, Takashi Saito, Takeshi Ota

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## SMART biochar technology for remediation of toxic metals in soils

Mahtab Ahmad, Avanthi Igalavithana, Sang Soo Lee, Anushka Rajapaksha, Yong Sik Ok*

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## Monitoring of radiocesium contamination in farmland soil in eastern Japan

Kazunori Kohyama*, Yasuke Takata

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## Mitigation of radioactive contamination from farmland environment and agricultural products

Takuro Shinano

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## Development of low-Cd rice by mutation with ion-beam

Satoru Ishikawa

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## Effect of iron plaque and rice genotypes on As accumulation in rice plants grown in As-contaminated paddy soils

Chien-Hui Syu, Pei-Yu Jiang, Chia-Chen Huang, Chia-Hsing Lee, Dar-Yuan Lee*

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## Comparison of various single chemical extraction methods for predicting the bioavailability of arsenic in paddy soils

Woo-Ri Go, Seon-Hee Jeong, Anitha Kunhikrishnan, Gyeong-Jin Kim, Ji-Hyock Yoo, Namjun Cho, Kwon-Rae Kim, Kye-Hoon Kim, Won-Il Kim*

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Cd and As contamination of agricultural products and countermeasures in Japan

Tomohito Arao1*, Tomoyuki Makino1, Satoru Ishikawa1, Masaharu Murakami1, Kaoru Abe1, Koji Baba1, Noriko Yamaguchi1, Megumi Sugiyama1, Akira Kawasaki1, Tadashi Abe1, Yuji Maejima1, Ikuko Akahane1, Shingo Matsumoto2

1 National Institute for Agro-Environmental Sciences, Kannondai 3-1-3, Tsukuba, Ibaraki 305-8604, Japan.
2 Shimane University, 2059 Kamihonjomachi, Matsue, Shimane, 690-1102, Japan
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Abstract: Many heavy metals exist in minute amounts in natural agricultural soil. However, when their amounts exceed a certain level due to pollutants brought from outside, soil contamination occurs and agricultural products become contaminated. There have been many cases in Japan of heavy metal contamination originating from old mines and smelters, and soil contamination of agricultural land has become a social issue. In particular, cadmium (Cd) is one of the most harmful heavy metals. If agricultural products absorb an excessive amount of Cd, they may adversely affect people’s health, and therefore allowable concentrations are regulated by law. If agricultural land has become contaminated with Cd, measures for minimizing the absorption of Cd by agricultural crops are necessary; these include: (1) soil dressing, (2) water management (paddy field), (3) chemical cleaning of soil, (4) phytoextraction, and (5) use of different varieties and rootstock.

Rice consumption is not only a major source of Cd but also that of arsenic (As) for the population of Asia. Flooding of paddy fields is effective in reducing grain levels of Cd; however, anaerobic conditions in paddy soil lead to As mobilization and, therefore, As uptake by rice could increase. A new study has been launched investigating whether As and Cd concentration in rice grains can be lowered simultaneously by controlling irrigation water and by using a rice cultivar with low Cd uptake, along with agricultural materials.

Key Words: Cd, As, rice, chemical washing, phytoextraction

1. Introduction

After the first metal mine in Japan began operating in the early eighth century, metal mining became an established industry between the late sixteenth and early seventeenth centuries, and especially during the Edo period (1603–1867) when many metal mines were developed (Arao et al., 2010). However, it was not until the Meiji Era (1868–1912) when Japanese metal mines started to be run as modern businesses; major mines were scaled up through direct management by the national government. Among various metals mined, there was a remarkable increase in the demand for copper (Cu) and zinc (Zn) as raw materials for general and military industries, and so the production outputs of mines increased dramatically. After the end of World War II, further demand for metals was driven by rapid economic growth in the 1960s. Enormous quantities of metal ore were mined and smelted to meet this demand, yet domestic output alone could not keep pace and increasing quantities had to be imported from overseas. During this historical process, various heavy metals were released into the environment, causing extensive soil contamination by toxic metals such as cadmium (Cd).

The three heavy metals designated by the Agricultural Land Soil Pollution Prevention Law (1970) of Japan as specified toxic substances are Cu, Cd, and arsenic (As). Past incidents of acute soil contamination with these three metals include the following. The Ashio Copper Mine Mineral Pollution incident—in which Cu spilled from the Ashio Copper Mine and contaminated the soils of paddy and upland fields along the Watarase River in the middle of the Meiji Era—is regarded as the beginning of Japan’s problems with pollution.

Another example was itai-itai disease, which occurred in the lower reaches of the Jinzu River and was caused by Cd that had leaked into the river from the Kamioka Copper Mine upstream (Toyama Prefectural Itai-itai Disease Museum, 2012). Thereafter, Cd contamination of agricultural land along rivers with a mine upstream caused problems at several locations in Japan. Furthermore, smoke emitted by Zn and Cu smelters into the atmosphere contaminated neighboring agricultural land with Cd. In another case, As compounds that spilled from some mines in Kyushu and the northern part of the Chugoku region contaminated nearby agricultural land, damaging the paddy rice and the health of the local population that relied on contaminated well water.

The Japanese government has been investigating the quantities of these metals present in agricultural soil and their concentrations in agricultural crops, and has been implementing...
countermeasures using the soil dressing method through the Special Land Improvement Project for Pollution Prevention, etc. The heavy metal responsible for the most serious contamination of agricultural land is Cd. Today, there are few new cases of soil contamination by Cd from mines and smelters because of strict regulations and management by law. Countermeasures have been completed in most of the Cd polluted sites. But low Cd polluted field exits around these sites.

Cd is toxic to humans at concentrations lower than those at which it is toxic to plants because its effects on humans are cumulative. A health-based guidance value for Cd of 25 μg kg⁻¹ bodyweight per month was established by the JECFA (2010), and a ML of 0.4 mg kg⁻¹ for Cd in polished rice has been adopted by the Codex Alimentarius Commission. Rice is a staple crop in Asia and is also the principal source of dietary intake of Cd in the Japanese population; therefore, minimizing the intake of Cd from rice is an important health goal. Although flooding of paddy fields effectively reduces grain levels of Cd (Masui et al. 1971; Otake 1992; Ogawa 1994; Yamada et al. 1971), anaerobic conditions in paddy soil lead to As mobilization which could consequently increase the uptake of As by rice (Koyama, 1975).

The Ministry of Agriculture, Forestry, and Fisheries of Japan analyzed the As content of staple crops in Japan and found that an average value of total As and inorganic As concentration in polished rice were 0.14 mg kg⁻¹ and 0.12 mg kg⁻¹, respectively (2014). As concentration in most other agricultural products was below the detection limit. Although sea food is a common source of total As, most of As in sea food are organic form which is less toxic than inorganic As. A market-basket survey, with As-speciation analysis, indicated that rice is a major source of dietary intake of inorganic As in the Japanese population (Oguri et al. 2014). The intake of inorganic As in rice carries a significant risk for cancer in populations for whom rice is a staple food. In some cases, human intake of inorganic As from the consumption of rice exceeds that from drinking water. A ML for inorganic As (0.2 mg kg⁻¹) in polished rice has been adopted by the 37th Session of the Codex Commission (2014).

A new study has been launched investigating whether As and Cd concentration in rice grains can be lowered simultaneously by controlling irrigation water and by using a rice cultivar with low Cd uptake, along with agricultural materials.

2. Countermeasures against Cd contamination of agricultural crops

2.1. Soil dressing

Soil dressing is a very effective soil improvement method that prevents agricultural products from being contaminated with Cd. It involves covering the contaminated agricultural soil with uncontaminated soil (Yanagizawa et al. 1984; Yamada 2007). There are several ways of improving polluted soils by soil dressing. As of 2012, 91.0% of the total polluted land (7,592 ha), designated by the Agricultural Land Soil Pollution Prevention, was remedied by applying uncontaminated soil and/or replacing the soil (MOE 2013).

However, if the soil dressing is not sufficiently thick, the roots of rice will reach the contaminated soil, decreasing the effect of the countermeasure. Experiments conducted to date show that the required thickness of soil dressing is 20–40 cm, depending on the soil, method, and environment. If the land is cultivated too deeply, causing mixing with contaminated soil, or if the Cd content in irrigation water is high, the effect of soil dressing will decrease over time.

While soil dressing is very effective for reducing Cd absorption by paddy rice, many problems have been pointed out with the method. The biggest problem is the cost: the unit cost of soil dressing is very high, and so the method is impractical without imposing a large penalty on the responsible party or without a sufficiently large federal subsidy (Otake 1992). Second, soil dressing materials are difficult to procure: it is no longer easy to obtain large quantities of high-quality mountain soil that contains an appropriate amount of clay. In addition, soil dressing causes a decline in soil fertility on paddy fields, because the mountain soil used for soil dressing is often sterile, containing little humus. Therefore, it is necessary to restore soil fertility by applying large quantities of organic fertilizers for many years. In addition, soil dressing raises the paddy surface, making it necessary to construct levees and improve irrigation and drainage facilities.
2.2. Water management and control of Cd absorption by paddy rice using a combination of materials

When a paddy field is flooded and the soil is under reducing conditions, hydrogen sulfide will be generated, which equilibrates with sulfate ions. The hydrogen sulfide is dissociated into sulfide ions depending on the pH and precipitates with cadmium ions as cadmium sulfide (CdS), which is less soluble in water as shown by its low solubility product (Ksp = 5.0 x 10^{-28}).

However, when the field is drained and the soil is under oxidative conditions, CdS is ionized to form cadmium sulfate (CdSO₄), which is soluble in water (Ito and Iimura 1976). This means that the solubility of Cd changes depending on the redox potential (Eh) of the soil (Iimura and Ito 1978), and the Eh of paddy field soil can be controlled through water management. Consequently, it is possible to control Cd absorption by paddy rice through water management. Therefore, Cd absorption by paddy rice is suppressed by filling the paddy field with water to prevent the soil from drying and thus reducing the amount of Cd released into the water. Several studies on the effects of water management on Cd absorption by paddy rice confirm that it is possible to control the Cd content in brown rice through water management during the growing period (Masui et al. 1971; Otake 1992; Ogawa 1994; Yamada et al. 1971).

Furthermore, if the soil pH changes to neutral, Cd bonds with phosphate ions or carbonate ions and becomes less soluble in water. An increase in pH enhances the cation exchange capacity (CEC) of the soil, which has a variable charge and increases the Cd ion adsorption to clay.

Therefore, Cd absorption by paddy rice can be suppressed by applying a material that increases the pH of the soil, such as calcium carbonate, calcium silicate, autoclaved lightweight concrete (ALC), or fused silicate phosphate (Otake 1992; Ogawa 1994; Hasegawa et al. 1995; Yamada et al. 1973). However, if the soil acts as a strong buffer, application of materials may not be sufficient to increase the pH of the soil. For such soil, the control of Cd absorption by paddy rice through the application of materials may be limited and sometimes close to zero. Thus, a combination of material application and the aforementioned water management technique is used to enhance the control of Cd absorption by paddy rice (Otake 1992).

2.3. Chemical washing method for contaminated soil

Soil washing is a remediation technology that involves mixing contaminated soil with a washing material in liquid form, extracting contaminant from the soil, and then processing the extract containing Cd in a purification system. This chemical method can be used to remove the contaminant effectively and restore the soil for a relatively short period. Although studies on washing-based soil remediation have been conducted by several private companies, many of these studies targeted old factory sites, etc., and involve transporting contaminated soil to processing facilities for purification, where both the volume of contaminated soil and its Cd content are reduced by separating the clay fraction, which has a higher concentration of heavy metals. However, it is difficult to apply these methods to paddy fields.

In order to apply the washing method to paddy fields, the following need to be completed: (1) selection of washing materials that have a low environmental burden, high efficiency, and low-cost; (2) development of an onsite washing and drainage treatment system; (3) ensuring good soil fertility and crop growth; and (4) maintenance of the washing effect. A washing method that addresses these issues and is applicable to paddy fields is described below.

Examination of optimum washing conditions in a preliminary test, ferric chloride was selected as a washing agent and the optimum washing conditions using this material were examined (Makino et al. 2006; Makino et al. 2008). When ferric iron chloride is added to the water in a paddy field, the dissociated iron ions that may form hydroxide precipitate with the release of protons, thus reducing the pH of the water and eluting Cd:

In order to optimize soil washing for paddy fields, it is necessary to examine various conditions such as the amount of washing agent applied, soil–water ratio, agitation time, material washing cycles,
and water washing cycles. As for the soil–water ratio, the larger is the liquid phase fraction, the more efficient is the removal of Cd. However, due to the height of paddy field levees and the structural limitations of the tractors used in the washing process, the soil–water ratio should be approximately 1:2. Although the Cd extraction rate increases with the number of material washing cycles, there should be only one material washing cycle in consideration of the amount applied on-site and the Cd removal effect. In order to reduce the residual chlorine concentration to a nontoxic level (500 mg l⁻¹ or lower), there should be three or more water washing cycles and the chlorine concentration should be monitored on-site during the work.

In previous studies on washing contaminated soil, tests were conducted on local paddy fields using hydrochloric acid (Takijima et al. 1973) or EDTA (Nakasima and Ono 1979) and the effect was confirmed. However, the on-site processing of the wastewater left after washing had not been examined for a Cd-contaminated paddy field. In order to apply washing technology to paddy fields, on-site treatment of wastewater from the washing process is required. In other words, after the on-site washing process is completed using the aforementioned optimum washing conditions, Cd in the wastewater should be collected and removed using on-site wastewater processing facilities.

The procedure was as follows (Fig. 1):

Fig.1 Procedure of on-site chemical washing

(1) the local Cd-contaminated paddy fields were materialwashed (to extract Cd from the soil) and then (2) waterwashed (to remove residual Cd and chlorine), and finally, (3) the wastewater was processed (to collect and remove Cd from the wastewater using an on-site wastewater treatment system employing a chelating agent).

After water-wash cycles, the concentration of residual chlorine in the paddy field water was lower than 500 mg l⁻¹, the level at which chlorine is considered to begin affecting the growth of crops. The Cd concentration in the wastewater after washing with ferric chloride and water can be reduced to lower than the effluent standard (0.1 mg l⁻¹) and the environmental standard for water quality (0.003 mg l⁻¹) by collecting and removing Cd using an on-site wastewater treatment system (Takano and Makino 2006; Makino et al. 2007).

The Cd content in the washed soil in the area measured using the 0.1 mol l⁻¹ hydrochloric acid extraction process was reduced to 20–40% of that in the unwashed area (Cd reduction rate of 60–80%), confirming that this washing method effectively removes Cd.

As some soil properties, such as exchangeable potassium, exchangeable magnesium and pH, had been changed after the soil washing, they can be corrected by applying fertilizers.

The washing process had very little effect on the growth and yield of paddy rice, and although certain changes in soil fertility do occur, fertilizers can correct them. Thus, we conclude that this
washing method does not adversely affect soil fertility or the growth of paddy rice to a significant degree (Takano and Makino 2006; Makino et al. 2007).

The Cd concentration in brown rice dramatically reduced after the washing treatment to 30–40% of that in the nonwashed area (Takano and Makino 2006; Makino et al. 2007). The total cost of the chemical washing method depends on the Cd concentration of soil and other factors, and is estimated to be approximately 60% of that of soil dressing.

Akahane et al. (2013) evaluated the effects of soil washing with ferric chloride (FeCl₃) on Cd concentrations in soil solutions and Cd absorption by two spinach cultivars in pot experiments. Soil washing with FeCl₃ affected the exchangeable cations (i.e. calcium increased and magnesium decreased). The Cd concentration in the soil solution from washed plot was lower than that in the solution from the unwashed plot throughout the spinach growth period, which was attributed to the exchangeable Cd content in both soils, because the fraction equilibrated with the Cd concentration in the soil solution. The exchangeable cation composition was affected by soil washing, but no significant difference in spinach yield was observed between the washed and unwashed plots. The leaf Cd concentration in the two spinach cultivars was up to 70% lower in the washed soils. This study suggested that soil washing in rice paddy fields with FeCl₃ was effective for controlling the Cd absorption risk of upland crops such as spinach.

2.4. Purification technology based on phytoextraction

Phytoextraction has been studied in the US and in Europe as a method of preventing soil and groundwater pollution. This technology aims to purify the environment by utilizing the functions of plants. For some time now, it has been known that some plants can efficiently absorb Cd in soil. For example, tall goldenrod (Solidago altissima L.) in the composite family and pennycress (Thlaspi caerulescens L.) in the brassica family (Brown et al. 1995; Hammer and Keller 2003) are considered to be able to absorb large amounts of Cd. However, these plants may not be suitable for large-scale phytoextraction because they are small and grow slowly, and has basal rosettes of leaves, making them difficult to harvest mechanically.

To Select plants to be used in phytoextraction, Ishikawa et al. (2006) grew leaf mustard (Brassica juncea L.), maize (Zea mays L.), sugar beet (Beta vulgaris L.), and rice (Oryza sativa L.) in pots filled with two kinds of Cd-contaminated soil (gray lowland soil and ando soil) for 1 month. The rice and sugar beet planted in both soils showed the highest level of Cd absorption in their aboveground parts. Since sugar beet is a cold-climate crop, they concluded that rice was the most appropriate purifying plant.

Murakami et al. (2007) selected maize (Zea mays L.), soybean (Glycine max (L.) Merr.), and rice (Oryza sativa L.) as the major crops grown in paddy fields and upland fields converted from paddy fields in Japan. These plants were grown in pots filled with three kinds of Cd-contaminated soil (two kinds of gray lowland soil and one kind of ando soil) for 2 months. Soybean and rice showed the highest level of Cd absorption. Since soybean defoliates after the blooming stage, rice was the most promising purifying plant in Japan.

As rice does not have replant failure and has an established growing system and mechanized harvesting system, rice is considered to be the most appropriate plant to be used for the phytoextraction of paddy fields. Moreover, it has been discovered that not only the Japonica-Indica hybridized variety but also certain kinds of the Indica variety have a high-Cd-absorption ability (Arao and Ae 2003). The variety Cho-ko-koku has been selected as a candidate phytoremediator for paddy fields contaminated with low to moderate levels of Cd, and a field trial of phytoextraction by using this cultivar has been launched. (Murakami et al. 2009). The heavy metal ATPase 3 (OsHMA3) was identified as the gene that controls root-to-shoot Cd translocation rates in Cho-ko-koku (Miyadate, et al., 2011).

In order to achieve commercialization of phytoextraction technology, the aforementioned varieties of rice with a high-Cd-absorption ability as well as efficient harvesting of Cd-containing rice plants, on-site drying, packaging, storage, and transportation of such rice plants, and safe treatment of absorbed Cd are important. To address these challenges, Murakami et al. (2010) have (1) established
an integrated mechanized system of harvesting, on-site drying, and packaging of Cd-containing rice, and (2) developed an efficient system for collecting Cd involving the incineration of the harvested rice plants. The integrated system, from harvesting grown rice to incineration, is shown in Fig. 2.

Fig. 2 Pytoremediation for Cd-contaminated paddy soils by High-Cd-accumulating rice

In a paddy field with good drainage conditions, to ensure on-site drying, rice plants should be harvested using a combine harvester that separates rough rice and straw. The straw should be sun-dried and rolled for collection. In contrast, in a paddy field with poor drainage, the rough rice and straw should be harvested together using a self-propelled whole crop harvester, and then rolled, collected, and stored under a moisture-permeable waterproof sheet (sheet that lets internal moisture pass through to the outside but does not allow rainwater from the outside through to the inside) in the field for about 2 months (Taniguchi 2006; Murakami 2007; Ibaraki and Taniguchi 2007).

Next, it is necessary to efficiently and safely collect the Cd contained in the harvested rice. For this purpose, an incineration system has been developed that incinerates dried rice, volatilizes most of the Cd in the harvest as metallic ions, captures them with a bug filter, collects nearly the whole amount as fly ash, and leaves no Cd in the main ash (incinerated ash), preventing the discharge of effluent gas.

In an incineration test, when harvested rice was incinerated at higher than 900°C inside the incinerator, there was no unburned matter, and the Cd collection rate from fly ash was 99.6%. The Cd concentration in the effluent gas was lower than 0.01 mg kg⁻¹, with almost no release into the atmosphere (Taniguchi 2006; Ibaraki and Taniguchi 2007).

While phytoextraction is a low-cost, environment-friendly method, it is time-consuming. Since it is difficult to recover Cd-contaminated soil in a single step by phytoextraction, two to four applications (harvests) may be necessary.

In a test conducted in three local fields, phytoextraction by the Indica rice varieties grown for 2–3 years without irrigation after drainage reduced the soil Cd content by 18–38%, and reduced the grain Cd content in subsequently grown Japonica food rice by 39–50% (Murakami et al. 2009; Honma et al. 2009; Ibaraki et al. 2009). The total cost of the phytoextraction method depends on the Cd concentration of soil and other factors, and is estimated to be less than one-seventh of that of soil dressing.

The world rice core collection (WRC), consisting of 69 accessions which covers the genetic diversity of almost 32 000 accessions of cultivated rice, was also used to select candidate for phytoremediator, and Jarjan (WRC28), Anjana Dhan (WRC30) were found (Uraguchi et al. 2009).
Abe et al. (2013) have developed new high-Cd-accumulating practical rice lines with non-shattering derived from gamma ray mutation from Jarjan, and Anjana Dhan.

2.5. Use of different varieties and rootstock

It has been known for some time now that the Cd-absorption capability of paddy rice differs from variety to variety. If grown in the same environment, the Japonica variety such as Koshihikari generally has a lower Cd concentration than the Indica variety, which is a long-grain rice (Arao and Ae, 2003).

Energetic heavy-ion beams have been recently used to generate mutants in higher plants because they induce mutations with high frequency at a relatively low dose, and they induce a broad spectrum of phenotypes without affecting other plant characteristics. Carbon ion-beam irradiation produced three rice mutants with <0.05 mg Cd·kg⁻¹ in the grain compared with a mean of 1.73 mg Cd·kg⁻¹ in the parent, Koshihikari (Ishikawa et al. 2012). There were no apparent differences in plant or grain morphologies between Koshihikari and low Cd mutants, and there were no significant differences in grain and straw yield and even in eating quality. Mutants produced by ion-beam radiation are not transgenic, so they are more likely to be accepted by consumers. Low cadmium Koshihikari mutant-2 is applied for the registration of commercial cultivar as Koshihikari-kan-1 (Fig. 3).

![Fig.3 Morphologies of plant and rice grains of Koshihikari-kan-1 and WT Koshihikari.](image)

It has also been found that with soybean, the Cd absorption ability and Cd concentration in the fruit body differ depending on the variety (Arao et al. 2003; Ishikawa et al. 2005; Sugiyama 2007), and this research is expected to result in the development of a new low-Cd-absorption variety. Significant inter-cultivar differences of soybean seed Cd concentrations arise from the inter-cultivar differences in root Cd accumulation ability. The Cd concentration in the shoots of plants at the vegetative stage is already controlled by the roots Cd concentration in the same way that it determines seed Cd concentration (Sugiyama et al. 2010).

Eggplant (Solanum melongena) fruits in Japan tend to have higher Cd concentrations than international maximum limits for fruiting vegetables. Grafting onto the Solanum torvum cultivars reduced Cd concentrations of eggplant fruits by about 1/2 to 3/4 compared with grafting onto eggplant or self roots (Takeda et al. 2007; Arao et al. 2008). For some vegetables including tomato, grafting is a useful tool to cope with problems of soil-borne diseases. If there is a rootstock, which translocates low Cd from root to shoot in commercially available rootstocks, it would be a practical method for reducing the Cd concentration of vegetables by grafting onto the rootstock.

Physiological properties involved in the differences in shoot Cd accumulation among rice cultivars (Uraguchi et al. 2009) and between Solanum species (Mori et al. 2009) were characterized. Cd was allocated in the central cylinder for Solanum melongena and localized around the endodermis...
for *Solanum torvum* (Yamaguchi et al. 2011a). The results demonstrated that the xylem loading process is a major factor in determining shoot Cd accumulation in both rice and Solanum species.

Ishikawa et al. (2011) have visualized and quantitatively analysed the real-time Cd dynamics from roots to grains in typical rice cultivars that differed in grain Cd concentrations. by the positron-emitting tracer imaging system (PETIS), and revealed that the high-Cd accumulating rice cultivars were characterized by rapid and abundant Cd transfer to the shoots from the roots, a faster transport velocity of Cd to the panicles, and Cd accumulation at high levels in their panicles, passing through the nodal portions of the stems where the highest Cd intensities were observed.

In rice nodes, the diffuse vascular bundles, which enclose the enlarged elliptical vascular bundles, are connected to the panicle and have a morphological feature that facilitates xylem-to-phloem transfer. Elemental maps of Cd, Zn, Mn, and S in the vascular bundles of node I were obtained by synchrotron micro-X-ray fluorescence spectrometry and electron probe microanalysis (Yamaguchi et al. 2012). The results provide evidence that transport of Cd, Zn, and Mn is differentially controlled in rice nodes, where vascular bundles are functionally interconnected.

Genetic analyses of shoot Cd accumulation have been reported in rice (Ishikawa et al. 2010; Ishikawa et al. 2012) and Solanum species (Yamaguchi et al. 2010). Such genetic information will be useful in developing efficient new varieties with low Cd trait.

### 2.6. A simple and quick on-site test for trace levels of Cd in food

Measuring Cd concentrations in plants is costly and troublesome, because it requires expensive analytical instruments for such procedures as ICP-OES, ICP-MS, or flameless atomic absorption spectrophotometry. These methods also require the services of analytical experts and the use of exhaust systems that can remove the toxic gases produced during acid digestion.

Recently, an immunochromatographic assay kit for detecting Cd in rice was developed by Kansai Electric Power Co. of Japan (Tawarada et al., 2003; Sasaki et al., 2007). This method uses the antigen–antibody complex reaction between the Cd–EDTA complex and an anti-Cd–EDTA antibody that reacts specifically with this complex to detect Cd at concentrations of 0.01 mg L\(^{-1}\) or higher; the results are read by the degree of color developed on a test paper. Cd in brown rice was extracted with HCl, and the extract was purified on a chelate silicagel column to remove other metals. The pretreated solution was then diluted with buffer for neutralization and tested with the immunochromatographic assay (Abe et al., 2006).

Cd extracted with HCl from wheat grain and fresh eggplant was purified sufficiently using an ion-exchange column treatment. Appropriate HCl extraction rates and dilution rates for the column eluate were selected; Cd concentrations in wheat grain and fresh eggplant were determined successfully by immunochromatography with respect to the international standards of 0.2 mg kg\(^{-1}\) and 0.05 mg kg\(^{-1}\) fresh weight, respectively (Abe K et al., 2011). Approximate Cd concentrations in wheat grain and fresh eggplant can be monitored easily and quickly by this method at locations where facilities for acid digestion and precision analysis are not available.

Abe et al. (2014) conducted an interlaboratory study to evaluate the kit for determining Cd in wheat, rice and soybeans and the results indicated that the kit was an inexpensive, reliable tool for quick and easy on-site determination of Cd in wheat, rice and soybeans.

### 3. Countermeasures against As contamination of agricultural crops

#### 3.1. Bioavailability of arsenic in soils and its uptake by crops

It is well known that damage by As tends to occur more in paddy rice than other upland crops. In the 1970s and 1980s, the mechanism of As damage of 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 the oxidative state to suppress the dissolution of As.

Ishizuka and Tanaka (1962) reported that 60–80% of 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).

Elevated As concentrations in rice and the soil solution result from changes in soil redox conditions, influenced by the water management practices during rice cultivation. Microscale changes in redox conditions from rhizosphere to soil matrix affect the As speciation and Fe-plaque deposition. In order to focus on the rhizosphere environment, Yamaguchi et al. (2014) observed microscale distribution and speciation of As around the rhizosphere of paddy rice with 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 the soil matrix. As was scavenged by iron mottles originating from 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.

### 3.2. Effects of water management on As and Cd content in rice grains

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 reducing grain Cd concentrations, but this treatment increased the As concentration considerably, whereas aerobic treatment during the same period was effective in reducing As concentrations but increased the Cd concentration markedly (Arao et al., 2009). Concentrations of dimethylarsinic acid (DMA) in grain 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.

When rice was grown under flooded conditions after the heading stage, DMA amendment to the soil resulted in higher DMA concentration in brown rice and rice straw (Arao et al., 2011). In the solution culture, not only DMA amendment but also MMA or arsenite amendment increased the DMA concentration 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 only 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 would be involved in the formation of DMA in brown rice.

As is highly mobilized when paddy soil is flooded, causing increased uptake of As by rice. Yamaguchi et al. (2011b) investigated factors controlling soil-to-solution partitioning of As under anaerobic conditions. Changes in As and iron (Fe) speciation due to 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 up to 80% of the total As in the soils. The solution-to-soil ratio of As(III) and As(V) (R(L/S)) increased with pH due to 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 soil to 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 redox reaction of As(V) to As(III) explained the different dissolution amounts of As in the two paddy soils. Anaerobic incubation for 30 d 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 the soil.
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 were 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.

3.3. Genetic diversity of arsenic accumulation in rice

As levels among Japanese cultivars may not influence dietary As exposure, because there was 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 comprising 69 accessions grown over a 3-year period (Kuramata et al. 2013). 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 total phenotypic variance in DMA was explained by the three QTLs.

3.4. Chromatographic separation of As species in rice

Various chromatographic separation modes are used for As speciation analysis, including anion-exchange, cation-exchange, reversed phase, ion-pair reversed phase, ion exclusion, and size exclusion. Baba et al. (2014) investigated HPLC conditions for As speciation analysis using a simple volatile mobile phase, isocratic elution, and silica-based pentafluorophenyl (PFP) columns, which are less expensive than polymer columns, such as the PRP-X100. The Discovery HS F5 column with a PFP stationary phase gave sharp peaks and full separation of the As species in 5 min, and other PFP columns showed lower performance. This separation method was applied to As species analysis in rice. The extraction of As from rice samples was performed using 0.15 M nitric acid. The methodology was validated by use of certified reference materials, NMIJ CRM 7503-a and NIST SRM 1568a, and extremely low As rice samples as blank samples.

4. References


Akahane I, Makino T, Maejima Y, Kamiya T, Takano H, Ibaraki T, and Inahara M. 2013. Remediation of cadmium-contaminated paddy soils by washing with ferric chloride (FeCl₃): Effect of soil washing on the cadmium concentration in soil solution and spinach, JARQ, 47:


quantitative trait locus for increasing cadmium-specific concentration in rice grain is located on the short arm of chromosome 7. J. Exp. Bot. 61:923-934.


The relationships of Cd concentration in arable soil and different rice varieties and the food safety evaluation of different brown rice varieties in Taiwan

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Abstract: A dataset from Taiwan that contains approximately 3000 paired soil and rice samples collected during 2006–2009 was used to derive SPT models. Each of the 3000 samples containing soil and rice analyses were taken from the same location to enable the derivation of the Cd concentration in specific variety rice grain prediction models. Coefficients of the CaCl₂ models for individual cultivars as well as for the pooled models for either Japonica or Indica cultivars are calculated. The similarity of the coefficients for different varieties suggests that the use of models based on pooled data for either Japonica or Indica cultivars in risk assessment seems justifiable. Differences between models based on pooled data from either Japonica or Indica cultivars, obviously, were pronounced. Higher levels of Cd in rice grains of Indica cultivars compared to Japonica cultivars are mainly reflected by the higher mode off-set (intercept) which ranges from 0.84 to 1.06 for Indica cultivars versus 0.51 to 0.72 for Japonica. These differences in Cd uptake between Japonica and Indica were mainly caused by higher Cd root to shoot transfer for Indica rather than differences in the uptake by the roots from soil. In Taiwan environment, for Indica cultivars, levels of national SQS50 should be reduced to 1 mg kg⁻¹ in clay and sandy soils to prevent excess uptake of Cd by brown rice. Cropping of Indica cultivars only can be recommended in soils without Cd pollution. For Japonica cultivars, national SQS50 levels should remain below 2 mg kg⁻¹ in slightly acid soils and 5 mg kg⁻¹ at neutral pH levels.

Keywords: Cadmium, Brown rice, Indica type, Japonica type, paddy field

Introduction
Taiwan government has taken various actions to considerably reduce the impact of heavy metals upon human health and the environment. Since 1982, different surveys of contaminated soils have been conducted by EPA of Taiwan. Cd, Pb, Zn, Cu, Cr and Ni are the most serious contaminants in the paddy rice fields and occur in the vicinity of irrigation channel or drainage ways. A total of 319 hectares of farmland have been completely surveyed and cleaned.

Paddy rice is the major stable crop in Taiwan. Due to industrialization, urbanization and the increase of traffic, soils have become polluted all over the world which has raised the concern on food safety and quality, also in Taiwan. To avoid unacceptable exposure of people to contaminants, safety limits in food have been set. The allowed maximum level of cadmium content in edible brown rice has been reduced to 0.4 mg kg⁻¹ in 2007. In Taiwan, several cases have been reported where the quality of rice did not meet the international standards. This has affected the consumer faith regarding the quality of rice in Taiwan. Levels of most contaminants, except Cd, have rarely caused concern sufficient to require changes in agronomic practice to minimize food-chain contamination. Compared to the other heavy metals, cadmium is relatively mobile and bioavailable in soils, so that transfer through the food chain is a major risk pathway (Australian government, 2005). As a consequence; it is harmful to human health. Also, it is potential toxic to biota at low concentration (Das et al., 1997).

It is generally believed that the chemical form of cadmium taken up by plants is the free uncomplexed Cd²⁺ ion present in soil solution. Any treatments or changes in soil conditions which affect the concentration of the Cd²⁺ ion will therefore affect plant accumulation of cadmium. Table 1 summarizes the factors listed by Chaney and Hornick (1978) that affect plant uptake of cadmium; this is also used by the Australian government (2005).

Past year, Taiwan agricultural authority had surveyed 341 rice samples of heavy metals in brown rice originating from the entire country. Average levels of heavy metals are: arsenic 0.17 mg kg⁻¹, cadmium 0.07 mg kg⁻¹, chromium 0.16 mg kg⁻¹, copper 2.48 mg kg⁻¹, mercury 0.001 mg kg⁻¹, nickel 0.54 mg kg⁻¹, lead 0.43 mg kg⁻¹ and zinc 39.2 mg kg⁻¹ (Lin, 1991). Taiwan FDA has analyzed 166 brown rice samples for heavy metals several years ago. Average levels of metals reported there are: cadmium 0.05 mg kg⁻¹ (ranging from below detection limit to 0.28 mg kg⁻¹, mercury 0.003 mg kg⁻¹.
(below detection limit to 0.009 mg kg\(^{-1}\)), and lead 0.03 mg kg\(^{-1}\) (below detection to 0.15 mg kg\(^{-1}\)) . Watanabe et al. (1996) showed that the lowest and highest geometric means of Cd contents in rice from Asia ranged from 2.67 to 55.7 g kg\(^{-1}\). Values for rice grown outside of Asia are 0.88 to 132.20 μg kg\(^{-1}\) respectively. These data show that, on average, the quality of rice is good. However, due to regional soil pollution, rice grown in specific areas (including the ones studied here) is of poor quality and the cadmium level in the rice is likely not to meet the national standards for cadmium in brown rice.

Due to limited waste water treatment, the quality of irrigation water in many Asian countries is sometimes rather poor. Sources of the pollutant load in irrigation water include those from sewage treatment plants, industry, mining, or the contribution from rivers draining metal-rice ore deposits. Other proposed methods include acid washing or heat treatment which is suitable for soils contaminated by cadmium, lead, and mercury. Some other treatment methods like the replacement of polluted soil by clean soil or a combination of different methods are proposed as well (EPA, 2004). Despite the efforts made and costs involved (the whole project costs were estimated at 10 million US dollar) still rice samples were found that did not meet the food quality standard this year.

The main reason for this is that even at moderate or low pollution levels, uptake by certain rice cultivars can be high. Also the impact of soil acidity, which is not considered in the soil test, plays an important role. Ideally soil standards to protect the quality of food should consider these issues as well. At present, there is a lack of information on how to incorporate the so-called availability of contaminants in soil policy. This study aims to investigate the differences between species and the relation between the availability (rather than the total amount in soil) and quality of rice.

### Heavy metals and food safety: the concept of availability in relation to plant uptake

Chaney (1980) introduced the concept of the “soil-plant barrier” and classified metals into four groups. Ag, Cr, Sn, Ti, Y and Zr were classified as the Group I elements, which pose little risk because they are not taken up to any extent by plants, which is mainly due to their low solubility in soil and, consequently, negligible uptake and translocation by plants. Group II includes the elements As, Hg and Pb which are strongly adsorbed by soil colloids, and while they may be absorbed by plant roots, they are not readily translocated to edible tissues, and therefore pose minimal risks to human health. Group III is comprised of the elements B, Cu, Mn, Mo, Ni and Zn, which are readily taken up by plants, but which are phytotoxic at the concentration that pose little risk to human health. Group IV consists of Cd, Co, Mo, and Se, which pose human and animal health risk at plant tissue concentration that are not generally phytotoxic. The elements that have most commonly given rise to health concerns about food safety are the heavy metals Cd, Hg and Pb, together with the anionic metalloids As and Se (Reilly, 1991).

To be available for uptake by plants, heavy metals must be present in the soil solution. There is considerable evidence that the chemical specification of heavy metals in solution affects their availability and toxicity to plants (Parker et al., 1995). For example, Cu\(^{2+}\) (Graham, 1981) and Cd\(^{2+}\) (Cabrera et al., 1988) have shown a high level of correlation with the activity of free metals ions in soil solution rather than with total elements concentrations in soils when plants uptake these metals. Soluble heavy metal concentrations in soils are likely to be influenced to some extent by the total concentrations of heavy metals present in soils. Thus in uncontaminated soils, heavy metal bioavailability is likely to be related to the nature of the soil parent material and the degree of soil weathering (McLaren, 2003). In case of contaminated soils, solution heavy metals concentrations are likely to increase with total contaminant loading. Colloids in soil that are able to sorb heavy metals will, therefore, have a major influence in controlling heavy metal availability to plants. Soil organic matter has a large capacity to sorb or complex heavy metals. In many studies organic matter has been shown to be a dominant soil constituent affecting sorption already a few decades ago, e.g., for Cu (McLaren and Crawford, 1973), Cd (Gray et al., 1998) and Hg (Yin et al., 1996). Heavy metals may also be sorbed by clay minerals and oxides of Fe, Al, and Mn, but these may play a relatively minor role in maintaining solution heavy metal concentrations compared to the overriding dominance of soil organic matter. The lack of significant correlations between heavy metal sorption and soil clay and oxide contents could be due to the low amounts of these constituents.

Soil pH has also been recognized as having a major influence on the availability of heavy metals that occur predominantly as cations (Cu\(^{2+}\), Co\(^{2+}\), Pb\(^{2+}\), etc.). The availability to plants is highest in acid
soils, and decreases as the soil pH increases due to sorption onto soil colloids or complexation with dissolved organic colloids.

The influence of soil pH on heavy metal availability is related to its effect on the reactions controlling heavy metal concentrations in the soil solution. Under acid conditions, sorption of heavy metal cations by soil colloids is at a minimum, and the solution concentrations are relatively high (McLaren, 2003). As soil pH rises, sorption of heavy metal cations increases and the solubility of oxides decreases. The sorption of heavy metals that occur in anionic forms decreases with increasing soil pH, and hence solution concentrations and availability increase.

It is generally believed that the chemical form of cadmium taken up by plants is the free uncomplexed Cd$^{2+}$ ion present in soil solution. Any treatments or changes in soil conditions which affect the concentration of the Cd$^{2+}$ ion will therefore affect plant accumulation of cadmium. Table 1 summarizes the factors listed by Chaney and Hornick (1978) that affect plant uptake of cadmium; this is also used by the Australian government (2005).

Table 1. Factors affecting cadmium uptake by plant from soil (Australian government 2005)

<table>
<thead>
<tr>
<th>Factors</th>
<th>Effects on Cd uptake by plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>soil</td>
<td></td>
</tr>
<tr>
<td>1. pH</td>
<td>Uptake increases as pH decreases</td>
</tr>
<tr>
<td>2. Soil salinity</td>
<td>Uptakes increases as salinity increases</td>
</tr>
<tr>
<td>3. Amount of Cd present</td>
<td>Uptake increases with concentration increases</td>
</tr>
<tr>
<td>4. Metal sorption by soil</td>
<td>Uptake decrease as sorption increase</td>
</tr>
<tr>
<td>a. Organic matter</td>
<td>Higher org. matter generally decreases uptake</td>
</tr>
<tr>
<td>b. Cation Exchange Capacity(CEC)</td>
<td>Higher CEC reduce s uptake</td>
</tr>
<tr>
<td>c. Clay, Fe and Mn Oxides</td>
<td>Presence decrease uptake</td>
</tr>
<tr>
<td>5. Micronutrients e.g. Zn deficiency</td>
<td>Increase uptake</td>
</tr>
<tr>
<td>6. Macronutrients: N, P, K</td>
<td>May increase or decrease uptake</td>
</tr>
<tr>
<td>7. Temperature</td>
<td>Higher temps. Increase uptake</td>
</tr>
<tr>
<td>8. Aeration e.g. flooding</td>
<td>Reduces uptake</td>
</tr>
<tr>
<td>Crop</td>
<td></td>
</tr>
<tr>
<td>1. Species and cultivar</td>
<td>Leafy vegs. &gt; root vegs. &gt; cereals &gt; fruits</td>
</tr>
<tr>
<td>2. Plant tissue</td>
<td>Leaf&gt; grain, fruit and edible root</td>
</tr>
<tr>
<td>3. Leaf age</td>
<td>Older &gt; Younger</td>
</tr>
<tr>
<td>4. Metal interactions</td>
<td>Presence Zn reduces uptake of Cd</td>
</tr>
</tbody>
</table>

Rice varieties and Cd uptake

Many reports showed that rice cultivars varied significantly with regard to Cd uptake and accumulation. Morishita et al. (1987) reported a comparative study on cadmium uptake by several rice cultivars in Andisols with a low total cadmium concentration in soil (0.102 mg kg$^{-1}$) in 1983 and 1985. It was observed that japonica brown rice varieties have the lowest average uptake rate compared to the other three varieties included, javanica, indica and Hybrid. Average cadmium levels in brown rice ranged from 2.1 to 27.0 µg kg$^{-1}$among 28 japonica varieties and from 4.1 to 55.5 µg kg$^{-1}$ among 23 indica varieties. Arao and Ishikawa (2006) reported that 49 varieties of rice were cultivated in Cd-polluted soils, the japonica varieties were categorized into the low grain Cd group. Several indica or indica-japonica varieties accumulated considerably amounts of Cd in grains as well as straw.
Some reports from China, however, seem to have an opposite result and indicated that *indica* varieties have lower uptake rates of cadmium compared to *japonica* varieties. Liu *et al.* (2003) conducted a study on 20 rice cultivars of different genotypes and origins by adding 100 mg kg\(^{-1}\) cadmium to the soil. The result showed that the effects of Cd on rice growth and development varied greatly among cultivars. Some varieties were highly tolerant to soil stress imposed by cadmium, while others were very sensitive. Differences existed among the cultivars for Cd uptake and distribution in rice plants, but the difference were not necessarily related to rice genotypes.

Liu *et al.* (2007) in an attempt to understand certain mechanisms causing the variations between rice cultivars with regard to Cd uptake and accumulation, conducted pot soil experiments with two rice cultivars at different levels of Cd, i.e., 0 (the control), 10, 50 mg Cd kg\(^{-1}\) soil. The results showed that the rice cultivar with higher concentrations of LMWOA (low-molecular-weight organic acids) in soil accumulated more Cd in the plants. The results indicate that LMWOA secretion by rice root, especially in Cd-contaminated soils, is likely to be one of the mechanisms determining the plant Cd uptake properties of rice cultivars.

### Soil assessment

At present the quality of soil is measured by the total metal content in the soil in Taiwan. This of course is a very practical and robust approach. Soil samples can be stored since the analysis is not affected by drying or other soil treatments. However, it has been shown that the total metal content in the soil and the uptake by arable crops are not always related to each other. In some soils the uptake of metals like cadmium is high even though the total metal content of the soil is low, even far below the current soil clean up values. After evaluating a range of different soil extractants such as weak electrolytes, organic acids, dilute mineral acids, chelating agents, ion-exchange resins and combinations of some of these, European countries propose to use extracts in dilute solutions of CaCl\(_2\) for assessing plant available Cd (Salt and Kloke, 1986). However, there is no agreement on the optimal soil/solution ratio, extraction times and concentration of CaCl\(_2\) (0.01-0.1 mM). Also, at present there are no ‘standards’ for cadmium measured in 0.01 M CaCl\(_2\). To evaluate the soil quality, one has to be able to compare the measured amount in the extract to a standard just like the control or action level. In the case of rice cropping this means that the study should allow deriving such ‘critical levels’ above which the food quality does not meet the food standards anymore.

In this study, to specifically derive soil quality standards for arable soils, the following points have to be considered:

1. Study the uptake of metals by different rice varieties: the relation between the soil and the crop therefore has to be established for all relevant cultivars
2. Study the relationship between the availability of cadmium in the soil as measured by CaCl\(_2\) and the uptake of the different rice varieties. Here we will test if such relationships exist and can be used to predict the uptake of cadmium by rice
3. Apply the results to make so-called risk maps showing areas where the soil quality is insufficient to grow rice that meets the food quality standard.

### Material and Methods

#### Field experiments

All experiments were carried out in existing paddy fields. In total, 8 different sites of heavy metals polluted (controlled sites by EPA) farmlands located at Chang-hua city (CH), Ho-mei town (HM) and Lu-kang town (LK) (24°05’N., 120°30’E) were selected to study the quality of soil and rice in 2005. In 2006, 4 additional sites of heavy metal-polluted (controlled sites of EPA) farmlands located at Tou-yuan (24°58’N., 121°18’E) and Hsin-chu city (24°48’N., 120°56’E.) were included to study the impact of highly cadmium polluted soil on cadmium uptake by rice. The sample collection and analysis procedures were similar as those described earlier for the Chang-hwa region.

Soil samples were collected from the root zone of each plant. It is important to take the soil and crop samples from the same location in order to be able to derive the relationship between soil quality and...
uptake by rice. Since the degree of pollution varies considerable within each field, 9 different sampling plots were established within each field along the pollution gradient. Because the uptake of different cultivars is also quite variable, each of the 9 sampling plots were further divided into 12 sub-sampling plots, one for each cultivar. In total 108 (9 x 12) soil and rice samples were thus collected from each field.

Rice plant tissue analysis

In 2005 and 2006, 12 cultivars of rice (as shown in table 2), including japonica and indica species as well as sticky rice, thus representing the 3 major rice varieties that at present are commonly cultivated in Taiwan were included in the study. The amount of N, P and K fertilizers were applied according to standard methods and regulations according to the fertilizer guidebook used by the farmers. Whole rice plants with root zone soils were harvested at maturity stage. After each root zone soil was sampled, the plants were washed thoroughly three times with tap water and three times with de-ionized water. The roots, stems, leaves, and grains were separated. The roots, stems, leaves were oven-dried at 70°C overnight. The grains were oven-dried at 60°C. The grain husks were removed mechanically using standard equipment. To avoid contamination by the grinding of the plant material, the oven-dried plant tissues were ground with pure titanium knives in standard grinders to reduce the size of tissue samples. The Cd, Cr, Cu, Ni, Pb, and Zn concentrations of the samples were determined by ICP-AES following HNO₃-HClO₄ (4:1) digestion procedures.

Table 2. The cultivars of rice used in the experiments in 2005 and 2006

<table>
<thead>
<tr>
<th>NO.</th>
<th>genotypes</th>
<th>Cultivars</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>japonica</td>
<td>Tainung No.70</td>
</tr>
<tr>
<td>2</td>
<td>japonica</td>
<td>Taikeng No.8</td>
</tr>
<tr>
<td>3</td>
<td>japonica</td>
<td>Tainung No.72</td>
</tr>
<tr>
<td>4</td>
<td>japonica</td>
<td>Kaohsiung No.143</td>
</tr>
<tr>
<td>5</td>
<td>japonica</td>
<td>Taitung No.30</td>
</tr>
<tr>
<td>6</td>
<td>indica</td>
<td>Tainung Sen No.20</td>
</tr>
<tr>
<td>7</td>
<td>japonica</td>
<td>Tainung No.71</td>
</tr>
<tr>
<td>8</td>
<td>japonica</td>
<td>Tainung No.67</td>
</tr>
<tr>
<td>9</td>
<td>indica</td>
<td>Tai Sen No.2</td>
</tr>
<tr>
<td>10</td>
<td>Hybrid indica (sticky rice)</td>
<td>Sen Waxy</td>
</tr>
<tr>
<td>11</td>
<td>indica</td>
<td>Taichung Sen No.10</td>
</tr>
<tr>
<td>12</td>
<td>japonica</td>
<td>Kaohsiung No.144</td>
</tr>
</tbody>
</table>

Results and discussion

Availability of metals in soil in relation to uptake by crops

The relationships that link cadmium in the soil to cadmium in the plant are based on the generally accepted view that metals are taken up by the plant from the soil solution. This means that ideally there is a relation between the metals in the soil solution (concentration or free metal ion activity) and the heavy metal levels in the plant (Brus et al., 2005). Usually this relationship is described using log-linear equations:

\[
\text{Log(Metal}_{\text{plant}}) = \alpha + \beta \cdot \text{Log(Metal}_{\text{soil solution}}) \quad [1]
\]

However, in many cases, screening of soils is still (and will be) based on the determination of the total metal content. Usually soil data like organic matter, clay and pH are also available. These data can also be used to predict the uptake of metals by rice because there is a close relation between soil properties and the metal content in the soil and the concentration in the soil solution (Römken et al., 2004):

\[
\text{Log(Metal}_{\text{soil solution}}) = \alpha_1 + \beta_1 \cdot \text{Log(Metal}_{\text{soil}}) + \gamma_1 \cdot \text{Log(OM)} + \delta_1 \cdot \text{Log(clay)} + \varepsilon_1 \cdot \text{pH} \quad [2]
\]

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The addition ‘1’ indicates that α and β in equation [2] differ from those in equation [1]. “OM” stands for organic matter, ‘clay’ for the percentage < 2μm. Also CEC can be used if available since, like OM and clay, CEC represents the binding capacity of the soil. Of course it should be kept in mind that the model is valid only within the range of soil properties and contamination levels that were used in to derive the model. If, for example the highest cadmium level in soil samples in the database is less than 2 mg kg⁻¹, the model cannot be used to predict uptake from soils that contain 15 mg kg⁻¹.

Finally equation [1] and [2] can be combined to predict the uptake by rice directly from soil properties without having to measure the soil solution (de Vries et al., 2007):

\[
\log(\text{Metal}_{\text{rice}}) = \alpha_2 + \beta_2 \cdot \log(\text{Metal}_{\text{soil}}) + \gamma_2 \cdot \log(\text{OM}) + \delta_2 \cdot \log(\text{clay}) + \varepsilon_2 \cdot \text{pH}
\]  

Again, the values for coefficient \(\alpha_2\), \(\beta_2\) etc. in equation [3] will be different from those in equation [2].

According to this concept, the regression equations to predict cadmium uptake by brown rice from soil properties according to equation [3] are presented in table3. The predicted cadmium content in several varieties thus calculated are compared to the measured ones in figure1. Different extracts for cadmium in soil were used to predict the uptake by rice, in this case aqua regia, \(\text{CaCl}_2\) and 0.1M HCL. The results indicate that the prediction of brown rice of cadmium concentration by considering soil pH, OM, CEC and Cd extracted by 0.01M \(\text{CaCl}_2\) is not always satisfactory which means among other that there are other soil factors or management activities that control the uptake by rice that need to be considered. In general however, the variability in the uptake of cadmium by rice can be explained rather well compared to standard methods that consider the metal content of the soil only.

Table3. Coefficients of the regression equation to predict cadmium in brown rice from soil properties and cadmium in soil (according to equation 1)

<table>
<thead>
<tr>
<th>cultivar</th>
<th>(R^2)</th>
<th>Intercept</th>
<th>pH</th>
<th>(\log(\text{OM}))</th>
<th>(\log(\text{CEC}))</th>
<th>(\log(\text{Cd}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tainung No.70</td>
<td>0.492</td>
<td>** -1.000*</td>
<td>0.129</td>
<td>-0.091</td>
<td>0.163</td>
<td>0.529*</td>
</tr>
<tr>
<td>Taikeng No.8</td>
<td>0.548</td>
<td>** -1.341*</td>
<td>0.156</td>
<td>-1.377*</td>
<td>1.338*</td>
<td>0.588*</td>
</tr>
<tr>
<td>Tainung No.72</td>
<td>0.480</td>
<td>** -1.030*</td>
<td>0.086</td>
<td>-1.132</td>
<td>1.190</td>
<td>0.567*</td>
</tr>
<tr>
<td>Koushung No.143</td>
<td>0.441</td>
<td>** -1.031*</td>
<td>0.037</td>
<td>-0.470</td>
<td>0.946</td>
<td>0.536*</td>
</tr>
<tr>
<td>Taitung No.30</td>
<td>0.463</td>
<td>** -1.116*</td>
<td>0.144</td>
<td>-1.385*</td>
<td>1.078</td>
<td>0.559*</td>
</tr>
<tr>
<td>Tainung Sen no 20</td>
<td>0.522</td>
<td>** -0.127</td>
<td>0.105</td>
<td>-0.881</td>
<td>0.547</td>
<td>0.643*</td>
</tr>
<tr>
<td>Tainung No.71</td>
<td>0.458</td>
<td>** -1.344*</td>
<td>0.171</td>
<td>0.390</td>
<td>-0.079</td>
<td>0.511*</td>
</tr>
<tr>
<td>Tainung No.67</td>
<td>0.113</td>
<td>** -0.975*</td>
<td>0.051</td>
<td>0.259</td>
<td>-0.188</td>
<td>0.241*</td>
</tr>
<tr>
<td>Tai Sen No.2</td>
<td>0.565</td>
<td>** -0.169</td>
<td>-0.043</td>
<td>-1.956*</td>
<td>1.955*</td>
<td>0.567*</td>
</tr>
<tr>
<td>Sen sticky rice</td>
<td>0.355</td>
<td>** -0.406</td>
<td>0.008</td>
<td>0.119</td>
<td>0.350</td>
<td>0.467*</td>
</tr>
<tr>
<td>Taichung Sen Np.10</td>
<td>0.343</td>
<td>** -1.399*</td>
<td>0.126</td>
<td>-0.258</td>
<td>0.696</td>
<td>0.453*</td>
</tr>
<tr>
<td>Kaohsiung No.144</td>
<td>0.377</td>
<td>** -0.870*</td>
<td>0.079</td>
<td>-1.186</td>
<td>1.160</td>
<td>0.580*</td>
</tr>
</tbody>
</table>

* = 5% significance level; ** = 1% significance level
1 soil organic matter (%);
2 Cation exchange capacity (cmol+/Kg)

Despite the fact that some of the models clearly need to be improved, some experimentally derived models were used to calculate so-called risk map for rice cropping. This was done by calculating the critical levels of cadmium in the soil above which the rice cadmium content exceeds the food quality standard. The soil database from Taiwan was used to compare this critical level with actual measured values across the country. Those areas where the actual cadmium content is lower than the critical
cadmium content are marked in red. This means that in these areas the quality of rice probably will not meet the food standard (see figure 3). The result indicates that areas exist where the quality of indica species will be insufficient (i.e., cadmium in the rice will exceed the standard of 0.2 or 0.4 mg kg\(^{-1}\)). Such areas include soils derived from marine sediment as well as polluted soils. One of the options that are rather easy to implement by farmers is to grow japonica genotype rice in these regions.

Figure 1. Measured versus predicted cadmium concentrations in brown rice using the equations shown in Table 3 based on CaCl\(_2\) extractable cadmium. Indica species are shown in the right hand columns.
Figure 2. Example of a risk map for cadmium for cultivar Tainun Sen 20 showing areas where brown rice will contain more than 0.2 mg kg⁻¹ Cd. The critical cadmium soil concentration is equal to 0.4 mg kg⁻¹.

Conclusions

The results from this study clearly demonstrate that the uptake of heavy metals, especially cadmium is related to the availability in soil. In the soils studied in 2005 and 2006, the availability was mainly controlled by soil pH and the total cadmium content of the soil. The availability can be measured quite accurately by 0.01 M CaCl₂. Using a combination of soil properties including pH, organic matter and CEC, the actual uptake by rice for different cultivars can be predicted rather well although the fit is different for different species. The results also show that in soils with low cadmium content, even below the current monitoring (2 mg kg⁻¹) or action value (5 mg kg⁻¹) used in Taiwan, the uptake of cadmium by indica species is too high. The quality of the rice does not meet the WHO or the FDA standards although the current soil quality standard is sufficient. This clearly illustrates the need for a revision of current standards used in Taiwan. A distinction between indica and japonica species is necessary since indica species have a high uptake and should not be cultivated on soils containing more than 0.4 to 1.0 mg kg⁻¹ cadmium. In contrast to this, some Japonica cultivars can be grown safely on soils that contain more than 5 mg kg⁻¹. Further testing of the relation between soil quality and uptake by rice is necessary to improve the development of soil quality standards that protect the general population from exposure due to cadmium uptake by rice.
References


The Relationships of Heavy Metals Concentration in Arable Soil, Rice Varieties and Vegetables and the Food Safety Evaluation of Agricultural Crop Production in Thailand

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Abstract: Soil resource is one of the effecting materials to grow edible plant. If soils are contaminated, their crop productivity and food may be contaminated with unsafe pollutants. Heavy metals are not easily to be decomposed in the natural condition. These pollutants are toxic and harmful to people health. Some areas in Thailand were contaminated with heavy metals. The major sources of contamination are from mining and industries. To know the whole picture of heavy metals contaminated in agricultural soil of Thailand and to evaluate edible crops for food safety and food security, soil samples were collected from arable land in 77 provinces and analyzed for physical and chemical properties such as texture, field moist, soil pH, organic matter and cation exchange capacities and heavy metals such as arsenic, cadmium, copper, lead and zinc. Plant samples such as rice and vegetables were also collected and analyzed for arsenic, cadmium, copper, lead and zinc. Heavy metals concentration in plants was evaluated for food safety by comparing with food standards. The results showed that physical and chemical properties of soil samples were as follow: Soil texture mostly was sandy loam and loamy sand. Soil moistures found in wide range, which were between 0.14 and 69.4 %. Soil pH found in the range of 3.8 to 9.4. Cation exchange capacities were varied between very low and very high. Organic matters were in the range of 0.01 to 6.90 %. Heavy metals concentration such as arsenic, cadmium, copper, lead and zinc were in the range of <0.003-64.0, <0.001-2.25, <0.013-89.6, <0.005-63.05 and <0.041-94.1 mg kg⁻¹, respectively. The average concentrations of these heavy metals were 5.8, 0.21, 12.43, 12.45 and 24.88 mg kg⁻¹ for arsenic, cadmium, copper, lead and zinc, respectively. Most of the data were below heavy metals background concentration. Some data were higher than background concentration but they were not exceeded the limit values for potentially toxic elements in soils in the European communities. Mean concentration of arsenic, cadmium, copper, lead and zinc in brown rice were 0.2, 0.03, 2.1, 0.2 and 18.2 mg kg⁻¹, respectively. Heavy metals concentration such as arsenic, cadmium, copper, lead and zinc concentrations in vegetables were in the range of 0.07-0.39, 0.03-0.27, 3.29-11.33, 0.19-0.89 and 31.1-61.47 mg kg⁻¹, respectively. The edible crops were safe when compare with the standards.

Keywords: Arable soil, Food safety, Heavy metals, Rice, Vegetables.

1. Introduction

Thailand has a land area of 51.31 million hectares where the area of 20.85 million hectares or about 41% are used for agriculture. There are 5.8 million farms or about 23 million farmers and agriculture GDP are 12.39% of total GDP. Therefore soil is important as the primary production input for agriculture. Good agricultural crop quality can be come from good soil quality. If soil is contaminated with toxic substance, this will effect to agricultural product and will impact to human health. Heavy metals are toxic elements and are not easily to be decomposed in the natural condition.

Arsenic appears in three allotropic forms: yellow, black and grey; the stable form is a silver-gray, brittle crystalline solid. It can be found naturally on earth in small concentration. Humans may be exposed to arsenic through food, water and air. Organic arsenic usually is not poisonous to humans but may be poisonous to humans in high concentrations. In general, organic arsenic is usually far less poisonous than inorganic arsenic. People can be exposed to arsenic by inhaling it, by consuming contaminated foods, water, or beverages, or by skin contact. Long-term exposures to arsenic lower
than toxic levels can lead to skin changes (darkening or discoloration), whitish lines may appear in the
fingernails. Arsenic exposure over the long-term has been associated with the development of certain
cancer. Acute symptoms of toxic level of exposure to arsenic may include the following: vomiting,
abdominal pain, diarrhea, cardiac problems shock and death.

Cadmium is a soft silver-white metal that is found naturally in the environment. Most cadmium
released into the environment through mining and smelting and enters the food chain from uptake by
plants from contaminated soil or water. Cadmium can cause of harmful health effects. Eating food
with high levels of cadmium can irritate or bother stomach and causes diarrhea. Breathing cadmium
can irritate and damage the lungs and can cause death. The lower and long-term exposure to cadmium
can cause kidney damage and it can lead to the formation of kidney stones and affect the skeleton,
which can be painful and debilitating.

Lead is a very strong poison. When a person swallows a lead object or breathes in lead dust,
some of the poison can stay in the body and cause serious health problems. The symptoms of lead
poisoning may include: aggressive behavior, anemia, constipation, difficulty sleeping, headaches,
irritability, loss of previous developmental skins (in young children), low appetite and energy and
reduced sensations. Copper and zinc are plant limiting factor but may be toxic to plant and human
health in high concentration.

Some areas in Thailand were contaminated with heavy metals. The major sources of
contamination are from mining and industries. Therefore it is important to know the whole picture of
heavy metals contaminated in agricultural soil of Thailand for crop production planning in the aspect
of food safety and food security.

Objectives

1. To study heavy metals concentration in arable soil.
2. To study heavy metals uptake and accumulated by rice and vegetables.
3. To study the relationship of heavy metals in soil and eatable plant.
4. To evaluate the safety of agricultural crop.

2. Materials and Methods

2.1 Study area

To achieve heavy metals concentration in arable soil and heavy metals accumulated in rice,
vegetables and another economic crops, soil and plant samples from Land Development Regional
Office 1-12 were collected and analyzed for physical and chemical properties.

2.2 Analytical methods

Soil pH was determined in soil-to-deionized water of 1:1 (g mL⁻¹) (Peech, 1965), and electrical
conductivity (EC) was determined by saturation extract of soil sample (Bower and Wilcox, 1965). Soil
particle-size analysis was determined by pipette method (Reynolds, 1993). Organic matter was
determined by wet digestion (Walkley and Black, 1947), cation exchange capacity (CEC) was
measured using the ammonium acetate method at pH 7 (Chapman, 1965).

Plant samples were dried at 65 °C for 72 hr and ground for analysis. Soil samples were digested
with a mixture of HClO₄ : HNO₃ (2:1), plant samples were digested in 2:1, HNO₃ : HClO₄ using an
open tube digestion technique (Zacinas et al., 1983). The As content in the digested solution was
determined by using a Hydride Atomic Absorption Spectrophotometer and using Inductive Couple
Plasma Emission Spectroscopy (Perkin Elmer Optima 2100 DV) for Cd, Cu, Pb and Zn analysis (Hesse, 1971).

3. Results

3.1 Characteristic of the studied soil

The physical and chemical properties of soil samples in Land Development Regional Office 1-12 were as follow: soil bulk densities were between 0.85 and 1.87 g cm\(^{-1}\). Soil field moistures found in wide range, which were between 0.14 and 69.4 % by weight. Soil texture mostly was sandy loam and loamy sand. Soil pH found in the range of 3.8 to 9.4. Electrical conductivities were between 0.01 and 1.50 dS m\(^{-1}\). Organic matters were in the range of 0.01 to 6.90 %. Cation exchange capacities were varied between 0.7 and 71.1 cmol kg\(^{-1}\) which were between very low and very high (Table 1).

3.2 Heavy metals concentration in arable soil

Soil samples were analyzed for heavy metals. The results showed that arsenic, cadmium, copper, lead and zinc concentrations were in the range of 0.003-64.0, ≤0.001-2.25, ≤0.013-89.6, ≤0.005-63.05 and ≤0.041-94.1 mg kg\(^{-1}\), respectively (Table 2 and Fig. 1.). The average concentrations of these heavy metals were 5.8, 0.21, 12.43, 12.45 and 24.88 mg kg\(^{-1}\) for arsenic, cadmium, copper, lead and zinc, respectively. Most of the data were below heavy metals background concentration. Some data were higher than background concentration but they were not exceeded the limit values for potentially toxic elements in soils in the European communities (arsenic, cadmium, copper, lead and zinc are 20, 3, 100, 100 and 300 mg kg\(^{-1}\), respectively).
Table 1. Characteristics of the studies soils in Land Development Regional Office 1-12

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Unit</th>
<th>Region 1</th>
<th>Region 2</th>
<th>Region 3</th>
<th>Region 4</th>
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<th>Region 12</th>
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<tr>
<td>BD</td>
<td>g cm⁻¹</td>
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<td>0.89±1.65</td>
<td>0.95±1.71</td>
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<td>1.02±1.74</td>
<td>0.85±1.61</td>
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<td>(1.42±0.2)</td>
<td>(1.35±0.29)</td>
<td>(1.43±0.1)</td>
<td>(1.45±0.18)</td>
<td>(1.45±0.15)</td>
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<td>(1.23±0.21)</td>
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<tr>
<td>Filed moist</td>
<td>% by wt</td>
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<td>0.98-56.09</td>
<td>1.17-28.86</td>
<td>0.80-34.2</td>
<td>0.40-32.79</td>
<td>8.47-48.76</td>
<td>5.61-35.83</td>
<td>3.84-44.7</td>
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<td>1.29-37.26</td>
<td>13.18-53.2</td>
<td>16.61-69.4</td>
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<td>(27.44±15.18)</td>
<td>(19.80±11.33)</td>
<td>(12.75±7.64)</td>
<td>(9.75±6.28)</td>
<td>(11.50±6.53)</td>
<td>(17.67±9.46)</td>
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<td>(5.9±0.9)</td>
<td>(6.1±0.9)</td>
<td>(6.3±1.4)</td>
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<td>(4.9±1.6)</td>
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<td>EC</td>
<td>dS m⁻¹</td>
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<td>0.01-0.50</td>
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<td>0.02-0.14</td>
<td>0.02-0.34</td>
<td>0.01-0.28</td>
<td>0.02-1.50</td>
<td>0.02-0.96</td>
<td>0.02-0.44</td>
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<td></td>
<td></td>
<td>(0.23±0.24)</td>
<td>(0.07±0.07)</td>
<td>(0.11±0.29)</td>
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<td>(0.09±0.06)</td>
<td>(0.08±0.07)</td>
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<td>(0.08±0.06)</td>
<td>(0.14±0.13)</td>
<td>(0.06±0.19)</td>
<td>(0.12±0.11)</td>
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<td>OM</td>
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<td>0.3-2.9</td>
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<td>0.4-3.4</td>
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<td>(2.0±0.9)</td>
<td>(1.6±1.1)</td>
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<td>(0.9±0.5)</td>
<td>(0.9±0.06)</td>
<td>(1.8±1.0)</td>
<td>(2.2±0.7)</td>
<td>(1.6±0.7)</td>
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<td>(2.1±1.3)</td>
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<td>CEC</td>
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<td>1.1-12.4</td>
<td>0.7-26.3</td>
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<td>4.7-23.2</td>
<td>1.8-66.3</td>
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<td>(21.5±16.4)</td>
<td>(9.2±9.5)</td>
<td>(6.8±5.7)</td>
<td>(3.1±2.9)</td>
<td>(6.5±5.7)</td>
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<td>66</td>
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Table 2. Heavy metals concentration in Land Development Regional Office 1-12

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<th>Heavy metals</th>
<th>Unit</th>
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<tbody>
<tr>
<td>As</td>
<td>mg kg⁻¹</td>
<td>1.29-33.79</td>
<td>0.35-30.70</td>
<td>0.003-6.53</td>
<td>0.11-7.22</td>
<td>0.01-25.89</td>
<td>1.27-64.00</td>
<td>2.84-37.18</td>
<td>1.45-9.30</td>
<td>0.08-42.50</td>
<td>1.14-24.70</td>
<td>0.29-10.12</td>
<td>2.45-16.40</td>
</tr>
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<td>Cd</td>
<td>mg kg⁻¹</td>
<td>≤0.001-1.80</td>
<td>≤0.001-0.40</td>
<td>≤0.001-1.45</td>
<td>≤0.001-0.60</td>
<td>≤0.001-1.80</td>
<td>≤0.01-1.55</td>
<td>≤0.001-2.15</td>
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<td>≤0.001-0.65</td>
<td>≤0.001-2.25</td>
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<tr>
<td>Cu</td>
<td>mg kg⁻¹</td>
<td>1.20-39.00</td>
<td>0.40-89.60</td>
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<td>4.05-18.85</td>
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<td>Pb</td>
<td>mg kg⁻¹</td>
<td>2.45-26.30</td>
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<td>1.90-39.95</td>
<td>3.80-57.00</td>
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<td>5.00-51.35</td>
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<tr>
<td>Zn</td>
<td>mg kg⁻¹</td>
<td>5.70-94.10</td>
<td>4.15-70.50</td>
<td>3.90-72.15</td>
<td>2.70-79.15</td>
<td>≤0.041-54.95</td>
<td>2.50-64.95</td>
<td>11.05-66.90</td>
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<td>66</td>
<td>60</td>
<td>62</td>
<td>24</td>
<td>18</td>
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</tbody>
</table>
3.3 Heavy metals background concentration in soil of Thailand

Soil samples collected from Land Development Regional Office 1-12 and analyze for heavy metals. All the data was frequency distributed in class interval to determine heavy metals background concentration in agricultural soil and found that the background concentration of arsenic, cadmium, copper, lead and zinc are 30, 1.0, 45, 55 and 75 mg kg\(^{-1}\), respectively (Table 3).

Table 3. Heavy metals background concentration in soil of Thailand

<table>
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<tr>
<th>Heavy metals</th>
<th>mg kg(^{-1})</th>
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<td>Cd</td>
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<td>Cu</td>
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<tr>
<td>Pb</td>
<td>60</td>
</tr>
<tr>
<td>Zn</td>
<td>95</td>
</tr>
<tr>
<td>Hg</td>
<td>0.15</td>
</tr>
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</table>

3.4 Heavy metals concentration in agricultural crop

Plant samples such as rice, corn, sugarcane, cassava, cabbage, Chinese cabbage, Chinese kale, Chinese white cabbage, morning glory and yard long bean were collected from arable area and analyzed for heavy metals. Mean concentration of arsenic, cadmium, copper, lead and zinc in brown rice were 0.2, 0.03, 2.1, 0.2 and 18.2 mg kg\(^{-1}\), respectively. Heavy metals concentration such as arsenic, cadmium, copper, lead and zinc concentrations in vegetables were in the range of 0.07-0.39, 0.03-0.27, 3.29-11.33, 0.19-0.89 and 31.1-61.47 mg kg\(^{-1}\), respectively (Table 4).
Table 4. The mean values of heavy metals concentration in agricultural crop

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<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
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<tr>
<td></td>
<td>mg kg$^{-1}$</td>
<td></td>
<td></td>
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<tr>
<td>Rice</td>
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<td>2.10</td>
<td>0.20</td>
<td>18.2</td>
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<td>Corn</td>
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<td>0.02</td>
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<td>Sugarcane</td>
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<td>0.02</td>
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<td>0.03</td>
<td>1.40</td>
<td>0.30</td>
<td>7.60</td>
<td>95</td>
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<td>Cabbage</td>
<td>0.16</td>
<td>0.06</td>
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<td>0.23</td>
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<td>Chinese cabbage</td>
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<td>0.20</td>
<td>5.57</td>
<td>0.42</td>
<td>61.47</td>
<td>43</td>
</tr>
<tr>
<td>Chinese kale</td>
<td>0.13</td>
<td>0.27</td>
<td>4.56</td>
<td>0.25</td>
<td>46.23</td>
<td>42</td>
</tr>
<tr>
<td>Morning glory</td>
<td>0.32</td>
<td>0.17</td>
<td>5.83</td>
<td>0.73</td>
<td>49.04</td>
<td>34</td>
</tr>
<tr>
<td>Yard long bean</td>
<td>0.07</td>
<td>0.03</td>
<td>11.33</td>
<td>0.89</td>
<td>44.43</td>
<td>30</td>
</tr>
<tr>
<td>Standard for rice</td>
<td>0.2-0.7</td>
<td>0.2-0.4</td>
<td>10</td>
<td>0.2</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Standard for vegetables</td>
<td>0.5-2</td>
<td>0.05</td>
<td>10-20</td>
<td>0.1-1</td>
<td>5-100</td>
<td></td>
</tr>
</tbody>
</table>

Some agricultural crop were also collected from contaminated area and analyzed for heavy metals. Cadmium concentration in rice grown in cadmium contaminated soil ranged from $\leq 0.01$ to 5.96 mg kg$^{-1}$. Arsenic concentration in corn, sugarcane, yard long bean, morning glory, bean and mango were in the range of $\leq 0.001$ to 0.742 mg kg$^{-1}$, respectively (Table 5). Cadmium concentration in corn, sugarcane, yard long bean, morning glory, bean and mango were in the range of $\leq 0.001$ to 2.50 mg kg$^{-1}$, respectively. Copper concentration in corn, sugarcane, yard long bean, morning glory, bean and mango were in the range of $0.80$ to 30.5 mg kg$^{-1}$, respectively. Lead concentration in corn, sugarcane, yard long bean, morning glory, bean and mango were in the range of $\leq 0.005$ to 7.00 mg kg$^{-1}$, respectively. Zinc concentration in corn, sugarcane, yard long bean, morning glory, bean and mango were in the range of $\leq 0.04$ to 61.80 mg kg$^{-1}$, respectively.

Table 5. Heavy metals concentration in some agricultural crop in contaminated area

<table>
<thead>
<tr>
<th>Agricultural crop</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg kg$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice</td>
<td>-</td>
<td>$\leq 0.01$-5.96</td>
<td>-</td>
<td>$\leq 0.01$-5.96</td>
<td>-</td>
<td>532</td>
</tr>
<tr>
<td>Corn</td>
<td>0.05-0.56</td>
<td>0.05-0.2</td>
<td>1.9-30.5</td>
<td>0.35-2.65</td>
<td>5.35-29.85</td>
<td>15</td>
</tr>
<tr>
<td>Sugarcane</td>
<td>0.022-0.742</td>
<td>0.05-0.25</td>
<td>0.80-6.50</td>
<td>0.30-7.00</td>
<td>$\leq 0.04$-19.41</td>
<td>14</td>
</tr>
<tr>
<td>Yard long bean</td>
<td>0.005-0.072</td>
<td>$\leq 0.001$-0.15</td>
<td>6.10-15.75</td>
<td>$\leq 0.005$-2.0</td>
<td>15.40-40.25</td>
<td>5</td>
</tr>
<tr>
<td>Morning glory</td>
<td>0.211-0.544</td>
<td>0.30-2.50</td>
<td>3.60-11.25</td>
<td>0.35-0.60</td>
<td>34.40-61.80</td>
<td>3</td>
</tr>
<tr>
<td>Bean</td>
<td>$\leq 0.001$-0.68</td>
<td>$\leq 0.001$-0.15</td>
<td>3.80-11.25</td>
<td>0.05-1.10</td>
<td>5.65-36.05</td>
<td>27</td>
</tr>
<tr>
<td>Mango</td>
<td>$\leq 0.001$-0.609</td>
<td>$\leq 0.001$-0.3</td>
<td>1.35-12.25</td>
<td>$\leq 0.005$-0.4</td>
<td>1.50-20.05</td>
<td>10</td>
</tr>
</tbody>
</table>
4. Discussion

4.1 Relationship of heavy metals concentration in soil and agricultural crop

Heavy metals concentration in rice, sugarcane, cassava, and vegetables were plotted against heavy metals in different textural class of soil and also found the relationship between these data. The results showed that most data of heavy metals in soil did not have relationship to agricultural crop. Weak relationship of arsenic and cadmium in soil and rice were found (Table 6).

Table 6. Relationship of heavy metals in rice and soil

<table>
<thead>
<tr>
<th>Textural class</th>
<th>Arsenic</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>Y=0.019x-0.002, R²=0.273</td>
<td>Y=0.001x+0.011, R²=0.001</td>
</tr>
<tr>
<td>Silt clay loam</td>
<td>-</td>
<td>Y=0.251x-0.027, R²=0.168</td>
</tr>
<tr>
<td>Silt loam</td>
<td>Y=0.025x-0.012, R²=0.221</td>
<td>-</td>
</tr>
</tbody>
</table>

The relationship of arsenic in soil and cassava were found and in the order of sand>loamy sand>loam, the relationship of cadmium in soil and cassava were rather strong and in the order of sand>loam>clay. The relationship of zinc in soil and cassava were in the order of clay>loam>sand (Table 7).

Table 7. Relationship of heavy metals in cassava and soil

<table>
<thead>
<tr>
<th>Textural class</th>
<th>Arsenic</th>
<th>Cadmium</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>Y=0.004x-0.006, R²=0.144</td>
<td>Y=0.056x-0.012, R²=0.501</td>
<td>Y=0.238x-1.359, R²=0.657</td>
</tr>
<tr>
<td>Loam</td>
<td>Y=0.01x-0.031, R²=0.701</td>
<td>Y=0.309x-0.011, R²=0.547</td>
<td>Y=0.628x-4.328, R²=0.626</td>
</tr>
<tr>
<td>Loamy sand</td>
<td>Y=0.018x-0.020, R²=0.971</td>
<td>Y=0.040x-0.000, R²=0.994</td>
<td>Y=1.945x-4.205, R²=0.229</td>
</tr>
<tr>
<td>Sand</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The relationship of cadmium in soil and sugarcane were different and in the order of loamy sand>sand>silty clay loam. The relationship of copper in soil and sugarcane was found only in sandy soil (Table 8).

Table 8. Relationship of heavy metals in sugarcane and soil

<table>
<thead>
<tr>
<th>Textural class</th>
<th>Cadmium</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silt clay loam</td>
<td>Y=-0.077x+0.078, R²=0.311</td>
<td></td>
</tr>
<tr>
<td>Loamy sand</td>
<td>Y=0.270x-0.009, R²=0.832</td>
<td>Y=0.334x+1.256, R²=0.688</td>
</tr>
<tr>
<td>Sand</td>
<td>Y=0.009x+0.016, R²=0.333</td>
<td></td>
</tr>
</tbody>
</table>

The relationship of arsenic in soil and Chinese kale were rather strong and in the order of clay loam>silty clay>clay. The relationship of cadmium in soil and Chinese kale were also rather strong and in the order of clay loam>clay>silty clay. The relationship of copper in soil and Chinese kale were in the order of loam>silt clay loam>silty clay and the relationship of zinc in soil and Chinese kale were in the order of sandy loam>silt clay loam>silty clay (Table 9).
Table 9. Relationship of heavy metals in Chinese kale and soil

<table>
<thead>
<tr>
<th>Textural class</th>
<th>Arsenic</th>
<th>Cadmium</th>
<th>Copper</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>-</td>
<td>Y=-1.023x+0.540, R²=0.865</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Clay loam</td>
<td>Y=0.063x-0.506, R²=0.930</td>
<td>Y=0.446x+0.387, R²=0.910</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silty clay</td>
<td>Y=0.012x-0.046, R²=0.869</td>
<td>Y=0.441x+0.069, R²=0.692</td>
<td>Y=0.007x+3.171, R²=0.152</td>
<td>Y=0.007x+3.171, R²=0.152</td>
</tr>
<tr>
<td>Silt clay loam</td>
<td>Y=0.022x-0.028, R²=0.519</td>
<td>-</td>
<td>Y=0.177x+0.276, R²=0.430</td>
<td>Y=0.389x+12.18, R²=0.516</td>
</tr>
<tr>
<td>Loam</td>
<td>-</td>
<td>-</td>
<td>Y=0.177x+0.276, R²=0.430</td>
<td>-</td>
</tr>
<tr>
<td>Sandy loam</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Y=0.389x+12.18, R²=0.516</td>
</tr>
</tbody>
</table>

4.2 Food safety evaluation of agricultural crop

Heavy metal concentrations in the edible crops of arable soils were safe when compared with the standards for rice and vegetables as recommended by Codex and Chinese regulation (Table 4, Table 10). In all crops samples from contaminated area, arsenic, copper and zinc concentration were lower than maximum permissible limits in vegetables but some samples cadmium and lead concentration were exceeded the maximum limit. Highest levels of cadmium in crops were detected in rice and morning glory respectively. Whereas the lead concentration was found in sugarcane, corn and yard long bean respectively (Table 5, Table 10).

Table 10. Standard for heavy metals concentration in some agricultural crop

<table>
<thead>
<tr>
<th>Agricultural crop</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>Codex, National Bureau of Agricultural Commodity and Food Standards:ACFS</td>
</tr>
<tr>
<td>Rice/cereal</td>
<td>0.2-0.7</td>
<td>0.2</td>
<td>10</td>
<td>0.2</td>
<td>50</td>
<td>Chinese regulation</td>
</tr>
<tr>
<td>Leafy vegetables</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>Codex</td>
</tr>
<tr>
<td>Vegetables/fruit</td>
<td>0.5</td>
<td>0.05</td>
<td>10</td>
<td>0.1</td>
<td>5-20</td>
<td>Chinese regulation</td>
</tr>
<tr>
<td>Standard for food contaminant</td>
<td>2</td>
<td>-</td>
<td>20</td>
<td>1</td>
<td>100</td>
<td>Ministry of Public Health, Thailand</td>
</tr>
</tbody>
</table>

5. Conclusion

Results of the study showed that concentrations of heavy metals in agricultural areas varied widely among the different regions of Thailand. Most data were not exceeded the permissible limits in soil as recommended by EU. Therefore, the arable soil in Thailand is safety for planting.

Most data of heavy metals in soil did not have relationship to agricultural crop. Weak relationship of arsenic and cadmium in soil and rice were found. The relationship of arsenic and cadmium in soil and Chinese kale were rather strong. Arsenic, cadmium and zinc in soil were found relationship to cassava, cadmium and copper in soil were found relationship to sugarcane.
The edible crops of arable soils were safe. Heavy metal concentrations in agricultural crops were lower than the permissible limit in rice and vegetables as recommended by Codex, National Bureau of Agricultural Commodity and Food Standards:ACFS and China regulation. Highest levels in crops were detected in leafy vegetable such as Morning glory, Chinese white cabbage and Chinese kale grown in contaminated soil, therefore it is recommended that in contaminated area should not be grown leafy vegetable.

6. Acknowledgement

The authors wish to thank Prof. Dr. Zueng-Sang Chen, Department of Agricultural Chemistry, National Taiwan University for his guidance and encouragement. We also thank the division of soil analysis and the division of land use planning, Land Development Regional Office 1-12 for their assistance in soil sampling. This work was supported by Land Development Department, Ministry of Agricultural and Cooperatives.

7. References

Land Development Department., (2009), Report on Study and Database Development of Heavy Metal in soil which grown Economic Crop, Bangkok.
The relationships between Cd content in arable soils and different vegetables and the evaluation of food safety of vegetables in Taiwan

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Abstract: For better understanding the range of heavy metal concentration of vegetables, a survey of vegetables in major vegetable production areas was conducted by Taiwan Agricultural Research Institute (TARI) in cooperation with seven district agricultural research and extension stations (DARES) since 2008. In addition, with the funding of and coordinating with Environmental Protection Administration (EPA) of Taiwan, field experiments at Cd contaminated sites with soil Cd levels close to or above monitoring value of food crop farmland was conducted by TARI from 2010 to 2013 to investigate the difference of Cd contents in edible part of various vegetables as well as the effect of soil properties on Cd absorbed by vegetables. Results of survey indicated the percentage of vegetables from main production areas with Cd concentration of edible part exceeding regulation levels were merely 0.6% and with rare concern of food safety, while the percentage of vegetables from potentially Cd contaminated areas with Cd concentration of edible part exceeding regulation levels were up to 5.6%, presenting higher risk of Cd-contamination. Results of field experiments indicated the Cd accumulating ability was quite different in edible part of various vegetables. The Cd content of some vegetables exceeded regulation levels of vegetable and fruit crops even when soil Cd level was far lower than the intervention value. However, the Cd contents of sponge gourd, snap bean, and asparagus bean all complied with the regulated values when soil Cd reached the intervention value. With respect to food safety of agricultural produces and health hazards of people, a sound and cautiously designed program of arable land use in high-risky area is indeed quite needed.

Key Words: cadmium, vegetables, food safety

1. Introduction

Advanced with the development of industrialization, man-made pollutants such as most concerned heavy metals entered into food chain via environment and posed a threat to human health. Chaney (1980) introduced the concept of the "soil-plant barrier" and classified metals into four groups. Ag, Cr, Sn, Ti, Y and Zr are classified as the Group I elements, which pose little risk because they are not taken up to any extent by plants, which is mainly due to their low solubility in soil and, consequently, negligible uptake and translocation by plants. Group II includes As, Hg and Pb which are strongly adsorbed by soil colloids. While they may be absorbed by plant roots, they are not readily translocated to edible tissues, and therefore pose minimal risks to human health. Group III is comprised of B, Cu, Mn, Mo, Ni and Zn, which are readily taken up by plants. They are phytotoxic at concentrations that pose little risk to human health. Group IV consists of Cd, Co, Mo, and Se, which pose human and animal health risk at plant tissue concentration that are not generally phytotoxic.

To ensure the food safety in Taiwan, standards for the tolerance of Hg, Cd and Pb in rice and standards for Cd and Pb in vegetable and fruit crops were set by the Ministry of Health and Welfare (MHW) (Table 1). In addition, different regulatory standards of heavy metal pollutants, including Cd, of soil were set by Environment Protection Administration (EPA) for food crop farmland and other land, respectively (Table 2). Heavy metal in food crop farmland may lead to high exposure risk for human since food intake via the soil-plant-human pathway exists, so the regulatory standards of heavy metal pollutants in food crop farmland soil are stricter than that in other soil. Furthermore, the uptake and translocation of heavy metals is governed by factors such as soil properties, climate, crop characteristics and cultivation management. Nevertheless, the geological conditions and the diversity of climate in Taiwan could render rather complicated soil properties. Hence, incidents of soils with heavy metal contents fulfilling the regulation levels for food crop farmland but output rice or vegetables not conformed to the food regulation levels of heavy metals occurred now and then, for instances, rice, garlic beyond Cd limit, and rice beyond Pb limit.

As vegetables are indispensably important source of daily diet of Taiwanese, according to Daily Diet Guide (MHW, 2011) newly published by Ministry of Health and Welfare, it suggests rising the
consumption of vegetables and fruits while lowering that of fat, grain and rhizome foods. Therefore, the food safety of vegetables draw very highly concerns in Taiwan. However, past studies of heavy metal concentration of vegetables are very rare in Taiwan (Lin et al. 1992; Shih et al. 2008) with only the survey conducted by Lin et al. collected vegetable samples from major arable land in Taiwan. Regrettably, the Cd concentration of vegetables reported by Lin et al. (1992) is based on sorted groups of vegetables and lack of data of individual vegetable.

For better understanding the range of heavy metal concentration within vegetables, a survey of vegetables in major vegetable production areas was conducted by Taiwan Agricultural Research Institute (TARI) in cooperation with seven district agricultural research and extension stations (DARES) since 2008. In addition, with the funding of and coordinating with EPA, field experiments at Cd contaminated sites with soil Cd levels close to or above monitoring value has conducted by TARI from 2010 to 2013 to investigate the difference of Cd contents in edible part of various vegetables as well as the effect of soil properties on Cd absorbed by vegetables.

Table 1. Standards for the tolerance of Cd and Pb in some vegetable and fruit crops in Taiwan (MHW, 2011).

<table>
<thead>
<tr>
<th>Vegetable groups</th>
<th>Cd(mg kg⁻¹)</th>
<th>Pb(mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaf vegetables</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Head/flower vegetables</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td>Root/stem vegetables</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Bulb vegetables</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Gourd/fruit vegetables</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Legume Vegetables</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 2. Regulatory standards of Cd, Cu, Hg, Pb and Zn in soil of Taiwan (EPA, 2011).

<table>
<thead>
<tr>
<th>land use</th>
<th>Cd</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intervention value(mg kg⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Food crop farmland</td>
<td>5</td>
<td>200</td>
<td>5</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>Other land</td>
<td>20</td>
<td>400</td>
<td>20</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>Monitoring value(mg kg⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Food crop farmland</td>
<td>2.5</td>
<td>120</td>
<td>2</td>
<td>300</td>
<td>260</td>
</tr>
<tr>
<td>Other land</td>
<td>10</td>
<td>220</td>
<td>10</td>
<td>1000</td>
<td>1000</td>
</tr>
</tbody>
</table>

2. Survey on Cd concentration of vegetables

2.1 Survey on Cd concentration of vegetables in major vegetable production areas

The survey was corporately conducted since 2008 by seven DARESs with TARI, the former engaged in collecting samples from major production areas while the later was in charge of chemical analysis of samples. During January, 2008 to June, 2010, 1900 vegetable samples were collected, with sampled locations distributed as Fig.1 Among them, samples of different vegetables are 897 for leaf vegetables, 111 for head vegetables, 752 for root/stem vegetables (excluding bulb vegetables) and 140 for gourd/fruit vegetables, respectively.

As illustrated in table 3, the range of Cd concentration in edible part were ND to 0.151 mg kg⁻¹ for leaf vegetables, ND to 0.080 mg kg⁻¹ for head vegetables, ND to 0.116 mg kg⁻¹ for root/stem vegetables, and ND to 0.115 mg kg⁻¹ for gourd/fruit vegetables, respectively. Among them, the Cd level of all leaf vegetables and gourd/fruit vegetables were within the regulation levels of Cd for vegetable and fruit crops (MHW, 2011), while those exceeding tolerance levels were carrot of root/stem vegetables, Chinese cabbage of head vegetables, and iceberg lettuce of head vegetables, and the percentage of each vegetable with Cd concentration exceeding the regulation levels was 0.6%, 6.1%, and 9.8%, respectively. Overall, take the entire vegetables into account, the percentage of vegetables from main production areas with Cd concentration of edible part exceeding regulation...
levels were merely 0.6%, obviously with rare concern of food safety. Furthermore, compared to surveys of Wolnik et al. (1985) and Wiersma et al. (1986), the Cd contents of vegetables in Taiwan are not higher than those of United States and Netherland.

Fig. 1. A map of Taiwan showing locations (☆) of vegetable samples collected from major vegetable production area.
Table 3. Cd concentration of vegetables (values of maximum, minimum, mean and standard deviation) collected from major production areas and percentage of Cd exceeding the regulation levels in Taiwan.

<table>
<thead>
<tr>
<th>Vegetable group</th>
<th>Vegetable name</th>
<th>n</th>
<th>Moisture (%)</th>
<th>Min. (mg kg⁻¹ fresh weight)</th>
<th>Max. (mg kg⁻¹ fresh weight)</th>
<th>Mean (mg kg⁻¹ fresh weight)</th>
<th>SD (%)</th>
<th>Above the national standard (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaf vegetables</td>
<td>Pai-tsai</td>
<td>121</td>
<td>95.7</td>
<td>ND</td>
<td>0.115</td>
<td>0.023</td>
<td>0.018</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Spinach</td>
<td>18</td>
<td>93.0</td>
<td>0.048</td>
<td>0.133</td>
<td>0.079</td>
<td>0.022</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Mustard</td>
<td>86</td>
<td>94.6</td>
<td>ND</td>
<td>0.053</td>
<td>0.019</td>
<td>0.012</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Leafy lettuce</td>
<td>77</td>
<td>96.9</td>
<td>ND</td>
<td>0.073</td>
<td>0.019</td>
<td>0.016</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Water spinach</td>
<td>124</td>
<td>92.8</td>
<td>0.005</td>
<td>0.132</td>
<td>0.022</td>
<td>0.022</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Amaranth</td>
<td>25</td>
<td>93.9</td>
<td>0.008</td>
<td>0.050</td>
<td>0.021</td>
<td>0.009</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Pak-choi</td>
<td>101</td>
<td>94.8</td>
<td>ND</td>
<td>0.096</td>
<td>0.022</td>
<td>0.015</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ripe</td>
<td>24</td>
<td>95.4</td>
<td>0.010</td>
<td>0.044</td>
<td>0.023</td>
<td>0.009</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Velvet plant</td>
<td>31</td>
<td>92.6</td>
<td>ND</td>
<td>0.146</td>
<td>0.033</td>
<td>0.035</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ceylon spinach</td>
<td>16</td>
<td>93.1</td>
<td>0.005</td>
<td>0.055</td>
<td>0.027</td>
<td>0.014</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Garland chrysanthemum</td>
<td>20</td>
<td>95.0</td>
<td>ND</td>
<td>0.087</td>
<td>0.031</td>
<td>0.021</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Celery</td>
<td>26</td>
<td>94.7</td>
<td>0.011</td>
<td>0.151</td>
<td>0.037</td>
<td>0.026</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Green onion</td>
<td>228</td>
<td>92.2</td>
<td>ND</td>
<td>0.146</td>
<td>0.023</td>
<td>0.023</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Cabbage</td>
<td>49</td>
<td>93.5</td>
<td>ND</td>
<td>0.061</td>
<td>0.016</td>
<td>0.016</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>Iceberg lettuce</td>
<td>41</td>
<td>96.0</td>
<td>0.002</td>
<td>0.080</td>
<td>0.024</td>
<td>0.020</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>Chinese cabbage</td>
<td>21</td>
<td>96.2</td>
<td>0.004</td>
<td>0.042</td>
<td>0.015</td>
<td>0.012</td>
<td>0</td>
</tr>
<tr>
<td>Head vegetables</td>
<td>Radish</td>
<td>293</td>
<td>94.0</td>
<td>ND</td>
<td>0.079</td>
<td>0.017</td>
<td>0.011</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Carrot</td>
<td>329</td>
<td>89.7</td>
<td>ND</td>
<td>0.116</td>
<td>0.021</td>
<td>0.018</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Kohlrabi</td>
<td>18</td>
<td>93.5</td>
<td>ND</td>
<td>0.016</td>
<td>0.007</td>
<td>0.005</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Potato</td>
<td>100</td>
<td>79.5</td>
<td>ND</td>
<td>0.088</td>
<td>0.026</td>
<td>0.019</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ginger</td>
<td>12</td>
<td>94.3</td>
<td>ND</td>
<td>0.022</td>
<td>0.011</td>
<td>0.006</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Sponge gourd</td>
<td>100</td>
<td>95.2</td>
<td>ND</td>
<td>0.023</td>
<td>0.007</td>
<td>0.005</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Tomato</td>
<td>22</td>
<td>92.9</td>
<td>ND</td>
<td>0.044</td>
<td>0.008</td>
<td>0.014</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Cucumber</td>
<td>18</td>
<td>95.6</td>
<td>ND</td>
<td>0.115</td>
<td>0.010</td>
<td>0.011</td>
<td>0</td>
</tr>
</tbody>
</table>

Moisture of iceberg lettuce and mustard adopt from recent data of TARI, while that of ceylon spinach source from USDA, [http://www.nal.usda.gov/fnic/foodcomp/search/](http://www.nal.usda.gov/fnic/foodcomp/search/), and the remaining are from 'database of nutrient composition of food in Taiwan' published by Department of Health, Executive Yuan, R.O.C.

SD: standard deviation.
(Source: Lin et al. 2011)

2.2 Survey on Cd concentration of vegetables in potentially Cd contaminated areas

Potentially hazardous risks of arable land soil and crops may generated from impacts of human economical activities (Kachenko & Singh 2006; Nabulo et al. 2006). As limited acreage with huge population in Taiwan, aside from rural agricultural area, arable land still can be found scattering in industrial or urbanized area and their vicinity. From 2010 to 2011, to assess the Cd concentration and food safety in potentially Cd contaminated area, TARI cooperating with EPA launched a project surveying the Cd concentration of vegetables grown in selected arable soils of high Cd-containing. Three hundred and thirty seven vegetable samples were collected from high potentially Cd contaminated areas, including 197 leaf vegetables, 48 head vegetables, 55 root/stem vegetables, 10 gourd/fruit vegetables, and 27 legume vegetables, respectively.

In Table 4, the range of Cd concentration in edible part were ND to 0.482 mg kg⁻¹ for leaf vegetable, ND to 0.040 mg kg⁻¹ for head vegetables, 0.001 to 0.061 mg kg⁻¹ for root/stem vegetables, 0.001 to 2.261 mg kg⁻¹ for legume vegetables, and 0.011 to 0.117 mg kg⁻¹ for gourd/fruit vegetables, respectively. Among them, the Cd level of both head vegetables and root/stem vegetables were within the tolerance levels of Cd for vegetable and fruit crops (MHW, 2011), while those exceeding tolerance levels were kale of leaf vegetables, lettuce of leaf vegetables, peanut of legume vegetables, and eggplant of gourd/fruit vegetables, and the percentage of each vegetable with Cd concentration...
exceeding the regulation levels was 10%, 3.2%, 45.8%, and 71.4%, respectively. Overall, take the entire vegetables group into account, the percentage of vegetables collected from potentially Cd contaminated areas with Cd concentration exceeding tolerance levels of Cd for vegetable and fruit crops were up to 5.6%. Obviously, vegetables produced from potentially Cd contaminated areas present higher risk of food safety than those from major vegetable production areas.

Table 4. Cd concentration of vegetables (values of maximum, minimum, mean and standard deviation) collected from potentially Cd contaminated areas and percentage of Cd exceeding the regulation levels in Taiwan.

<table>
<thead>
<tr>
<th>Vegetables</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>SD</th>
<th>Percentage exceeding</th>
<th>Regulation level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaf vegetables</td>
<td>0.2</td>
<td>0.482</td>
<td>0.047</td>
<td>0.062</td>
<td>0.062</td>
<td>0.047</td>
</tr>
<tr>
<td>Head vegetables</td>
<td>0.1</td>
<td>0.001</td>
<td>0.013</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>Root/stem vegetables</td>
<td>0.1</td>
<td>0.001</td>
<td>0.022</td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
</tr>
<tr>
<td>Legume Vegetables</td>
<td>0.2</td>
<td>2.261</td>
<td>0.496</td>
<td>0.641</td>
<td>11</td>
<td>40.7</td>
</tr>
<tr>
<td>Gourd/fruit vegetables</td>
<td>0.1</td>
<td>0.117</td>
<td>0.055</td>
<td>0.039</td>
<td>5</td>
<td>50</td>
</tr>
</tbody>
</table>

3. Field experiments of Cd absorption by vegetables at Cd contaminated sites

Survey data collected from both major vegetable production areas and potentially Cd contaminated areas indicated the cadmium accumulating ability of various vegetables was quite different. In addition, vegetables grown at potentially Cd contaminated areas posed higher possibility of exceeding the regulation levels of vegetable and fruit crops than those grown at major vegetable production areas. Furthermore, rapid progress of breeding made by horticulturists results in multiply many varieties and cultivars of vegetables abundantly presenting on the markets. Therefore, it is of vital importance to investigate the Cd accumulating ability of various vegetables of daily diet in Taiwan for the policy decision making or planning of arable land use, so as to safeguard food safety of vegetable production. In the co-project of TARI and EPA during 2010 to 2013, field experiments were conducted to examine the effect of vegetable variety or cultivar on Cd accumulation when grown on selected fields with soil Cd concentration close to or above the monitoring value. Accompanied with vegetable sampling, the soils of root zones were sampled for the analysis of Cd to clarify the relationship between Cd content in soils and in edible part of vegetables, and the risk of exceeding regulation levels for different vegetables was also evaluated.

Field experiments were undertaken at sites located in Pade city (Taoyuan County), Dajia district (Taichung city), Houli district (Taichung city) and Huwei Township (Yunlin County) on a variety of soil properties and cadmium contents (Table 5). Average soil Cd content of Pade site was 7.19 mg kg⁻¹ and part of this site with Cd concentration exceeding the intervention value of Cd in soil for food crop farmland (Fig. 2). Average soil Cd contents of Houli and Dajie site were 3.16 mg kg⁻¹ and 1.63 mg kg⁻¹, respectively, and part of these two sites with Cd concentration exceeding the monitoring value (2.5 mg kg⁻¹). Though Cd content of Huwei site was lower than the monitoring standard and around 0.1 to 1 mg kg⁻¹, edibe part of garlics and peanuts with Cd content over tolerance levels has been produced in the past.

Table 5. Selected soil chemical properties and cadmium contents of experiment sites.

<table>
<thead>
<tr>
<th>Location</th>
<th>pHw</th>
<th>CEC</th>
<th>OM</th>
<th>Cd contents(mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cmol kg⁻¹</td>
<td>%</td>
<td>Min.</td>
</tr>
<tr>
<td>Pade</td>
<td>4.91</td>
<td>11.1</td>
<td>2.33</td>
<td>1.93</td>
</tr>
<tr>
<td>Dajie</td>
<td>6.74</td>
<td>8.36</td>
<td>3.80</td>
<td>0.48</td>
</tr>
<tr>
<td>Houli</td>
<td>6.15</td>
<td>7.69</td>
<td>1.41</td>
<td>2.36</td>
</tr>
<tr>
<td>Huwei</td>
<td>6.63</td>
<td>7.61</td>
<td>2.17</td>
<td>0.26</td>
</tr>
</tbody>
</table>
3.1 The Cd accumulating ability of vegetables and relationships between Cd concentration of soils and that of edible part of vegetables

The Cd concentration of edible part of all vegetables increased with soil Cd content raised, but the increased trends of Cd concentration of edible part of some vegetables become alleviated slow or no more when soil Cd content reached a certain level (Fig. 3 to Fig. 6). In addition, grouping phenomena were observed in the scattered plot of vegetable-Cd vs soil-Cd for part of vegetables (Fig. 3), while data points of part of vegetables are more scattered (Fig. 4). It suggested there are factors other than soil Cd content influencing Cd accumulation of vegetables.
Fig. 4. Relationship between Cd concentrations in soils and Cd concentrations in edible part of sweet potato vine.

In order to compare the Cd accumulating ability of vegetables, the effect of soil Cd concentration on Cd in edible part of vegetables was investigated by fitting a linear model, $y = a + bx$, for each vegetable separately (Table 6). Judging from the slope of regression analysis, amaranth was the most strong Cd accumulator among all vegetables tested. As with very strong power of heavy metal accumulation, amaranth usually serves as an ideal material for experiments of research and remediation of Cd contamination (Alamgir et al., 2011; Li et al., 2012). The Cd accumulating ability of other vegetables tested were in the order as water spinach > lettuce > carrot > Chinese cabbage > sweet potato vine > radish > cabbage > snap bean > tomato > sponge gourd > cucumber > asparagus bean. The edible part of asparagus bean was the weakest Cd accumulator among vegetables tested, and cucumber and sponge gourd were also weak Cd accumulator..

Table 6. Results of regression analysis$^z$ of Cd in edible part of vegetables and Cd in soils.

<table>
<thead>
<tr>
<th>vegetables</th>
<th>n</th>
<th>a</th>
<th>b</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweet potato vine</td>
<td>210</td>
<td>0.0185</td>
<td>0.0322</td>
<td>0.7585***</td>
</tr>
<tr>
<td>Water spinach</td>
<td>495</td>
<td>0.0213</td>
<td>0.1751</td>
<td>0.8674***</td>
</tr>
<tr>
<td>Amaranth</td>
<td>292</td>
<td>0.0533</td>
<td>0.5266</td>
<td>0.5286***</td>
</tr>
<tr>
<td>Chinese cabbage</td>
<td>323</td>
<td>0.0555</td>
<td>0.0582</td>
<td>0.7385***</td>
</tr>
<tr>
<td>Cabbage</td>
<td>317</td>
<td>0.0008</td>
<td>0.0199</td>
<td>0.9279***</td>
</tr>
<tr>
<td>Lettuce$^x$</td>
<td>208</td>
<td>0.1019</td>
<td>0.1438</td>
<td>0.4805***</td>
</tr>
<tr>
<td>Chinese cabbage</td>
<td>323</td>
<td>0.0555</td>
<td>0.0582</td>
<td>0.7385***</td>
</tr>
<tr>
<td>Cabbage</td>
<td>317</td>
<td>0.0008</td>
<td>0.0199</td>
<td>0.9279***</td>
</tr>
<tr>
<td>Lettuce$^x$</td>
<td>208</td>
<td>0.1019</td>
<td>0.1438</td>
<td>0.4805***</td>
</tr>
<tr>
<td>Radish</td>
<td>375</td>
<td>0.0032</td>
<td>0.0220</td>
<td>0.9222***</td>
</tr>
<tr>
<td>Carrot</td>
<td>423</td>
<td>0.0130</td>
<td>0.0628</td>
<td>0.9079***</td>
</tr>
<tr>
<td>Eggplant</td>
<td>95</td>
<td>0.0015</td>
<td>0.1427</td>
<td>0.7591***</td>
</tr>
<tr>
<td>Cucumber</td>
<td>98</td>
<td>0.0007</td>
<td>0.0061</td>
<td>0.8854***</td>
</tr>
<tr>
<td>Sponge gourd</td>
<td>186</td>
<td>0.0032</td>
<td>0.0067</td>
<td>0.9137***</td>
</tr>
<tr>
<td>Snap bean</td>
<td>81</td>
<td>0.0184</td>
<td>0.0124</td>
<td>0.5382***</td>
</tr>
<tr>
<td>Asparagus bean</td>
<td>66</td>
<td>0.0195</td>
<td>0.0048</td>
<td>0.3563***</td>
</tr>
</tbody>
</table>

$^z$Linear regression $y = a + bx$, $y = \text{Cd in edible part}$, $x = \text{Cd in soil}$

$^x$Denote $P < 0.001$

$^x$Including head lettuce and slightly heading lettuce
As to vegetable groups compared, leaf vegetables were with strong Cd accumulating ability, while legume vegetables and Gourd/fruit vegetables are weaker Cd accumulator. Table 4 also indicates even the same vegetable groups, different Cd accumulating ability observed in different individual vegetables. For instance, though leaf vegetables in general are with strong Cd accumulating ability, but sweet potato vine with Cd content in edible part obviously lower than other leaf vegetables. Lettuce is with Cd absorption ability obviously stronger than Chinese cabbage and cabbage in the same head vegetable group. What’s more, eggplant (a kind of solanaceous vegetables) is grouped as gourd/fruit vegetables according to vegetable/fruit groups reference table published by MHW, but Cd concentration of its upper part was just next to leaf vegetables. High Cd accumulating ability of solanaceous vegetables has also reported by Yang et al. (2010). According to research of Cd absorption ability of twenty eight vegetables conducted by Yang et al. (2010), Cd concentration in upper part (not specific in edible part) is in the order as leaf vegetables > solanaceous vegetables > kale vegetables > root vegetables > allimus > melon vegetables > legumes.

3.3 Difference of Cd accumulating ability among different cultivars of vegetables

Difference of Cd accumulating ability among different cultivars of many vegetables is not significant, for examples of water spinach, cabbage, radish, carrot (Fig. 5), and cucumber. However, there is significant difference of Cd accumulating ability among some cultivars of vegetables including lettuce (Fig. 6) and asparagus bean. For instance, four cultivars of lettuce involved with three slightly heading lettuce and one head lettuce were selected for field experiment, and great difference of Cd accumulating ability in edible part among different cultivars was observed. The Cd concentration of head lettuce and one slightly heading lettuce is much lower than the other two slightly heading lettuce, suggesting the Cd accumulating ability of lettuce was posibly related to its genotype and not to phenotype.

Fig. 5. Relationship between Cd concentrations of soils and Cd concentrations of edible part of carrot.
3.4 Relation of different soil Cd content with food safety of vegetables

For better evaluation of food safety of vegetables under current food crop farmland Cd intervention value 5 mg kg\(^{-1}\), all the vegetable samples collected from major vegetable production area, potentially Cd contaminated area, and field experiments at Cd contaminated sites were integrated to assess the possibility of exceeding the regulation levels of vegetable and fruit crops. The percentage of vegetables with Cd concentration of edible part exceeding regulation levels under different soil Cd contents (Table 7) indicated when soil Cd content reached 5 mg kg\(^{-1}\), the Cd concentration of edible part of amaranth, water spinach, Chinese cabbage, cabbage, lettuce, carrot and eggplant all exceeded regulation levels. Special attention should on cases of amaranth, Chinese cabbage, lettuce, and eggplant, they were already of concern and vulnerable to over regulation levels even when soil Cd content below 0.5 mg kg\(^{-1}\). However, cucumber at 4 mg kg\(^{-1}\), snap bean, asparagus bean and sponge gourd at 5 mg kg\(^{-1}\) of soil Cd content, respectively, all samples complied with regulation levels of Cd of vegetable and fruit crops, implicated low risk of Cd accumulated by these vegetables.

Table 7. The percentage of vegetables with Cd concentration of edible part exceeding regulation levels under different soil Cd contents.

<table>
<thead>
<tr>
<th>vegetables</th>
<th>n</th>
<th>(&lt;0.5)</th>
<th>0.5-1.0</th>
<th>1.1-2.0</th>
<th>2.1-3.0</th>
<th>3.1-4.0</th>
<th>4.1-5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaf vegetables</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sweet potato vine</td>
<td>210</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>6.5</td>
<td>10.0</td>
<td>62.5</td>
</tr>
<tr>
<td>Water spinach</td>
<td>495</td>
<td>0.0</td>
<td>13.6</td>
<td>69.2</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Amaranth</td>
<td>292</td>
<td>1.0</td>
<td>37.5</td>
<td>62.5</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Chinese cabbage</td>
<td>323</td>
<td>0.9</td>
<td>22.2</td>
<td>60.0</td>
<td>88.5</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cabbage</td>
<td>317</td>
<td>0.0</td>
<td>0.0</td>
<td>14.3</td>
<td>25.0</td>
<td>40.0</td>
<td>100</td>
</tr>
<tr>
<td>Lettuce(^2)</td>
<td>208</td>
<td>25.0</td>
<td>-(^2)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Head vegetables</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radish</td>
<td>375</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>12.5</td>
</tr>
<tr>
<td>Carrot</td>
<td>423</td>
<td>0.0</td>
<td>50.0</td>
<td>95.2</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Root/stem vegetables</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eggplant</td>
<td>95</td>
<td>5.9</td>
<td>85.7</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cucumber</td>
<td>98</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-(^2)</td>
</tr>
<tr>
<td>Sponge gourd</td>
<td>186</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
4. Conclusion

(1) The result of survey indicated the Cd concentrations of vegetables from main production areas exceeding regulated value of Cd ruled by Ministry of Health and Welfare were merely 0.6% with only rare concern of food safety, while those of potentially Cd contaminated areas were up to 5.6%, presenting higher risk of food safety.

(2) The results of field experiments indicated the Cd accumulating ability was quite different in edible part of various vegetables. Though cadmium content of some vegetables exceeded regulation levels of Cd of vegetable and fruit crops even when soil cadmium level far lower than stipulated intervention value of food crop farmland, the cadmium contents of sponge gourd, snap bean and asparagus bean all complied with vegetable regulation levels when soil cadmium reached intervention value.

(3) The results of field experiments suggested there were factors other than soil Cd content influencing Cd accumulating in vegetables. Therefore, further statistical analysis of soil and vegetable data has to be conducted to clarify the effect of soil properties on Cd absorbed by vegetables.

(4) With respect to food safety of agricultural produces and health risk of people, a sound and cautiously designed program of arable land use in high-risky area is indeed quite needed.

5. References


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

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Abstract: Codex Alimentarius Commission (Codex) has adopted the maximum permissible concentration of cadmium (Cd) in polished rice and other relevant crops, which requires an alleviation of the Cd contamination in rice grain. Various chemicals were tested for their Cd extraction efficiency by using three paddy soils, selecting ferric chloride (FeCl₃) as a promising chemical for on-site soil washing. The comparison of FeCl₃ extraction ability to that of various iron, manganese, and zinc salts revealed the primary extraction mechanism of FeCl₃ to be proton release coupled with hydroxide generation (hydrolysis). This indicates that proton release from FeCl₃ is controlled by the chemical equilibrium of hydroxide formation, and minimizes the negative effect on soil properties and environment, which are different from hydrochloric acid (HCl).

Washing with FeCl₃ led to the formation of Cd–chloride complexes, enhancing Cd extraction from the soils. We also developed in situ three-step washing method for Cd-contaminated paddy fields with FeCl₃. The method was comprised of 1) chemically washing the field soil with a FeCl₃ solution; 2) washing the treated soil with water to eliminate residual Cd and Cl⁻; and 3) on-site treatment of wastewater using a portable wastewater treatment system. Concentrations of Cd in the treated water were below Japan's environmental quality standard (0.01 mg L⁻¹). The on-site soil washing confirmed the effectiveness of FeCl₃ for decreasing Cd in soil and rice grains without negative effect on rice yield.

After the radioactive leakage from the Tokyo Electric Power Company’s Fukushima Dai-ichi nuclear power plant accident, widespread contaminated areas appeared where radioactive cesium in soil exceeds the provisional standard in Japan (5000 Bq/kg), and recovery from the contamination is an urgent issue. As radioactive cesium in undisturbed fields is initially accumulated in a very thin surface layer (roughly 0-2cm) in soil, removal of surface thin soil is effective in eliminating radioactive cesium. The removal of surface thin soil, however, could not apply for cultivated farmland. Thus, we have developed a new, cleaning method to remediate Cs-contaminated paddy fields by on-site stirring and cleaning (drainage of dispersed soil micro particle) of the surface layer of soil using water. The removal rate of Cs-137 from soil was 61.7% and can extensively decrease the amount of removed soil compared to the method of removal of contaminated surface soil.

Cs-137 concentration in brown rice cultivated in the decontaminated paddy field was reduced by 60%.

Key Words: cadmium, remediation, soil washing, rice, radioactive cesium, decontamination, soil agitation

1. Introduction

Japanese agricultural soils, in particular, paddy soils in some regions, have been heavily polluted with cadmium (Cd), owing to fast industrialization during the 1960s. The Japanese government enacted the Agricultural Land Soil Pollution Prevention Law in 1970 which demarcated Cd-contaminated paddy fields which produced rice grains containing more than 1 mg kg⁻¹. Since the Law was in effect, the polluted paddy soils have been remedied mainly by unpolluted soil dressing. However, Codex has adopted the maximum permissible concentration of Cd in polished rice (0.4 mg kg⁻¹), which requires an alleviation of the Cd contamination in rice grain. In addition, the soil dressing has become increasing difficult to implement because of its high cost and difficulty in obtaining unpolluted soil. Thus, it is a matter of urgency to develop promising technologies to remediate the Cd polluted paddy soils.

On-site soil washing could be one of the promising technologies, which is suitable for paddy fields which usually have an impervious layer that keeps the wash solution in the surface layer. For application of the soil-wash method to paddy fields, we have set up four points to guide the
development of potential on-site remedial technologies for Cd-contaminated paddy soils; (1) selection of chemicals that have low environmental impact but high efficiency, (2) development of an on-site washing and wastewater-treatment system, (3) ensuring favorable post-washing soil fertility and plant growth and (4) maintenance of the washing effect (Makino et al., 2007).

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

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

2. Theoretical Basis for Soil Washing Technologies

2.1 Adsorption and chemical forms of pollutants in soils

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

On the other hand, because radioactive cesium is strongly adsorbed by the frayed edge sites of soil colloids and by six-member silicate rings, radioactive cesium that has fallen on farmland stays in the superficial soil layer and very little moves to lower layers even after the rainy season.

The primary adsorption mechanism of organic pollutants is hydrophobic interaction on organic colloids. Coordination exchange, protonation, hydrogen bond, cation bridge and water bridge also work on the adsorption of organic pollutants.
Table 1 Chemical forms and sorption mechanisms of heavy metals in soils based on successive extractions.

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

2.2. Type of soil washing

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

2.3 Separation theory for size-fractionation of soil particle

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

3.1 Selection of washing chemicals

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

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

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

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Horizon</th>
<th>Depth cm</th>
<th>pH(H₂O)</th>
<th>pH(KCl)</th>
<th>*TCg/kg</th>
<th>*TNmg/kg</th>
<th>*TCdmg/kg</th>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand %</th>
<th>*Clay minerals</th>
<th>**Soil type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagano Ap</td>
<td>0-12</td>
<td>5.77</td>
<td>4.6</td>
<td>26.4</td>
<td>2.3</td>
<td>0.71</td>
<td>16.3</td>
<td>29.9</td>
<td>53.9</td>
<td>3.38</td>
<td>KI, Ch, Mi</td>
<td>Fluvaquents</td>
</tr>
<tr>
<td>Hyogo Ap</td>
<td>0-11</td>
<td>6.77</td>
<td>5.87</td>
<td>21.4</td>
<td>1.8</td>
<td>4.65</td>
<td>16.6</td>
<td>21.2</td>
<td>62.2</td>
<td>3.83</td>
<td>KI, Ch, Mi</td>
<td>Fluvaquents</td>
</tr>
<tr>
<td>Toyama Ap</td>
<td>0-10</td>
<td>4.96</td>
<td>3.87</td>
<td>15.6</td>
<td>1.4</td>
<td>1.21</td>
<td>15.3</td>
<td>17.6</td>
<td>67.1</td>
<td>1.11</td>
<td>KI-Ch-Sm, Ch, Sm</td>
<td>Epiaquepts</td>
</tr>
</tbody>
</table>

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

**Fig. 3. Efficiency of Cd extraction with various chemicals from the three soils.**

### 3.2 Extraction with metal salts

Same extraction procedure, as mentioned above, was conducted using the three soils and 100 mmol L⁻¹ of a variety of acids and metal salts, such as HCl, HNO₃, H₂SO₄, FeCl₃, MnCl₂, ZnCl₂, Fe(NO₃)₃, Mn(NO₃)₂, Zn(NO₃)₂, Fe₂(SO₄)₃, MnSO₄, and ZnSO₄. Various ions extracted using FeCl₃, Fe(NO₃)₃, and Fe₂(SO₄)₃ were determined by the following analytical methods with duplicate: ICP-OES for Na, K, Ca, and Mg, and distillation with MgO for NH₄⁺. An ion chromatograph (DX-320, Dionex Corp., USA) was used to measure anions (Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻). Dissolved organic carbon (DOC) was analyzed using a total organic carbon analyzer (TOC-5000, Shimadzu Corp., Japan). Visual MINTEQ software was used to analyze the ionic, DOC, and pH data sets to estimate Cd speciation in the extracts (Gustafsson, 2004).

The Cd extraction capacity was compared with other metal salts to elucidate the mechanism of Cd extraction by FeCl₃. The proportion of total soil Cd extracted by the washing chemicals (i.e., the Cd extraction efficiency) increased in the following order: Mn salts ≤ Zn salts << ferric Fe salts in all the three soils, with efficiencies ranging from 4-41%, 8-44%, and 24-66%, respectively (Fig. 4) (Makino et al., 2008). The amount of Cd extracted was negatively correlated with the extraction pH, suggesting that extraction pH plays an important role in determining the Cd extraction efficiency. When metal salts are added to soils, the dissociated metal cations that may form hydroxide precipitates with releasing protons according to the following equations (Hydrolysis):
\[ MmAn = mM^{n+} + nA^{m-} \]  \hspace{1cm} (1)

\[ M^{n+} + nH_2O = M(OH)_n + nH^+ \]  \hspace{1cm} (2)

\[ K_{m}^{m} = \frac{[M(OH)_n]^+ [H^+]^n}{[M^{n+}][H_2O]^n} \]  \hspace{1cm} (3)

where \( MmAn \) denotes a metal salt, \( M \) a metal cation (Fe, Zn, or Mn) and \( A \) an anion (Cl\(^{-}\), NO\(_3\)^{-}, or SO\(_4\)^{2-}\)). \( m \) and \( n \) represent the charge numbers of the anion and cation respectively. \( K_{m}^{m} \) denotes the equilibrium constants (expressed in terms of activities) for metal \( M^{n+} \) in Eq. (2), corresponding to \( 2.88 \times 10^{-4} \), \( 3.31 \times 10^{-13} \), and \( 6.46 \times 10^{-16} \) for Fe\(^{3+}\), Zn\(^{2+}\), and Mn\(^{2+}\), respectively (Lindsay, 1979).

The precipitation of the metal hydroxide (hydrolysis of the metal ion) generates protons at a rate that depends on \( K_{m}^{m} \), and these protons may decrease the extraction pH (Eqs. 1-3). Figure 5 illustrates the theoretical relationships between pH and activity of metal ions in the metal hydrolysis reactions at the equilibrium with soil iron (calculated using Eq. 3 and the \( K_{m}^{m} \) values). The pH of ferric hydroxide is around 2 (Fig. 5), which is much lower than the original soil-pH (H\(_2\)O) of the three soils. Thus, the Fe-hydrolysis is associated with a high decrease in soil pH compared to other two metals. This indicates that a driving force of the Cd extraction by FeCl\(_3\) is proton release, which results in a sharp decrease in soil pH. Heavy metal solubilization was greatly enhanced by acidification, and at pH 1.3, reached more than 80% of the total Cd content of the soil (Dube and Galvez-Cloutier, 2005). Our results and these previous reports endorse the effectiveness of iron salts as washing chemicals to remove soil Cd. Determination of the chemical speciation of Cd using MINTEQ software indicated that Cd–chloride complexes were formed, and this would enhance Cd extraction from the soils (data not shown).

**Fig. 4.** Comparison of cadmium extraction efficiency from the three soils by metal salts (gray bars) and strong acids (shaded bars). The extraction pH is shown in the parenthesis.

**Fig. 5.** Diagram of pH and metal activity to precipitate metal hydroxides
3.3 On-site soil washing at Cd-contaminated paddy field

An on-site testing plot (ca. 100 m²) was prepared in paddy fields in Japan. The soil-washing procedure consisted of three steps: (1) chemical washing with FeCl₃ solution, (2) following water washing to eliminate the remaining chemicals, and (3) on-site treatment of the wastewater by a portable purification system with a chelating material. Soil samples were taken from the washed and unwashed plots. 0.1 mol L⁻¹ HCl was used to extract soil Cd and the amounts of Cd extracted were determined by ICP-OES. Soil pH, electrical conductivity, total-C, total-N, available P, available N, and exchangeable cations were determined before and after soil washing. Rice plant was transplanted into the paddy field. Rice yields were measured after harvest. Part of the rice straw and some of the brown rice were ground, and digested with concentrated HNO₃ and then HClO₄. The Cd concentrations in the solutions were determined by ICP-OES.

During soil washing, the Cd concentration in the wastewater treated by the portable purification system was far below Japan's environmental quality standard (0.01 mg L⁻¹), proving that this technology was effective and promising for in situ treatment of wastewater. The Cl concentration was less than 500 mg L⁻¹ after three times' washing by water. This concentration is the threshold value for healthy rice crops.

The Cd content extracted with 0.1M HCl in the washed soils was 30-40% of that in unwashed soils (Cd reduction rate of 60–70%). The washing markedly decreased the Cd concentration. The pH(H₂O) and pH(KCl) of the soil were significantly decreased by on-site washing treatment. The soil EC increased with the treatment; however, it did not reach the critical level at which rice growth starts to retard. Exchangeable cations were decreased by soil washing. The Mg and K deficit was corrected by application of fertilizers to the washed soil. Total carbon and total nitrogen content were scarcely changed by washing.

Although changes in some relevant soil properties were observed, the changes can be easily corrected and does not affect relevant soil fertility. Soil washing considerably decreased the Cd content in the rice straw whose reduction rate were nearly reached around 70%, confirming availability of the soil washing method.

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

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

4.1 Particle size separation at a factory scale

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

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

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

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

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

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

(1) A test plot of approximately 100 m\(^2\) was created in a paddy. It was plowed to a depth of about 7 cm using a tractor equipped with a laser-leveling sensor.

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Fig. 6. An example of size fractionation of soil particle (Revised from Anderson et al., 1999)
The plot was flooded to a depth of 25 cm above the plow pan, sodium hydroxide pellets were added, the soil was agitated with cage wheels, and pH was adjusted to between 8 and 9.

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

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

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

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

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

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

The results are summarized below.

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

This method can also be applied to plowed rice paddies by adjusting the agitation depth.
5 Conclusions

We selected ferric iron chloride for soil washing on Cd contaminated paddy soils. We also revealed primary extraction mechanism of FeCl₃ is proton release coupled with hydroxide generation. We also developed an on-site soil washing technology for Cd-contaminated paddy fields. The washing had no negative affect on rice growth, and reduced the average Cd concentration in soil and rice grains.

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

Acknowledgements: The work on Cd and Cs were supported by grants from the Ministry of Agriculture, Forestry and Fisheries of Japan (Research project for ensuring food safety from farm to table AC-1311 and 1312, and Research project for Development of Decontamination Technologies for Radioactive Substances in Agricultural Land). The authors express the gratitude to all.

6. References

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SMART Biochar Technology for Remediation of Toxic Metals in Soils

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Abstract: Biochar is a carbon rich byproduct obtained from biomass pyrolysis. It has been known as a soil carbon enhancer or soil ameliorator. Heavy metal contamination is a serious concern in agricultural fields. Biochar showed significant positive impacts on heavy metal contaminated soils. Bioavailability of toxic metals such as Cd, Zn, Pb, Ni, and Cr can be reduced by biochar application into soils. Surface functional groups, cation exchange sites, and high porosity and surface area of biochar retain the heavy metals on its surface. However, some of toxic metals (Sb, As, Cu) demonstrated higher mobility in soils where biochar was applied. For instant, electrostatic repulsion between Sb and biochar surface enhances Sb mobility. High organic carbon content of biochar and reduction of As(VI) to As(III) can be factors increasing the mobility of Cu and As, respectively. All biochars are not equally effective for immobilizing metals in soils. Therefore, the development and selection of proper biochars is very important prior to its application on the large-scale contaminated sites. Research on biochar is contemporary and still needs in-depth investigations to determine the long-term effects of biochar. Therefore, smart biochar technology proposes a better or well-suitable way to remediate the soils contaminated with multi-metals via modification of typical biochar properties.

Keywords: Biochar, black carbon, heavy metals, soil remediation, immobilization, soil quality

1. Introduction

Biochar is defined as a carbon-rich product when biomass such as wood, manure or leaves is heated in a closed container with little or no available air (Lehmann and Joseph, 2009). In more technical terms, biochar is produced by so-called thermal decomposition of organic material under limited supply of O₂ at a relatively low temperature mostly below 700°C (Lehmann and Joseph, 2009). Because of its high organic C content, biochar has the potential to serve as a soil amendment to improve the physicochemical and biological properties of soils (Ahmad et al., 2014b). Biochar is also recognized as a very significant tool of environmental management (Lehmann and Joseph, 2009). Further information on the concept of biochar is well reported in a pioneering review by Lehmann et al. (2006). Four major areas where biochar is being used in environmental management include (i) soil improvement, (ii) waste management, (iii) climate change mitigation, and (iv) energy production (Lehmann and Joseph, 2009).

Inorganic contaminants, particularly toxic metals, in the environment originate mostly from a range of anthropogenic sources, such as mining, smelting, metal finishing, fertilizers, animal manure, pesticides, leaded gasoline, battery manufacture, power plants, waste water, and sewage sludge (Adriano, 2001; Lim et al., 2012; 2013). Unlike organic contaminants, those metals are non-biodegradable and their bioavailability makes them highly toxic to living organisms (Adriano, 2001; Abd El-Azeem et al., 2013; Ahmad et al., 2014b).

Numerous methods have been proposed to remediate toxic metals in soils. One of the most important technologies is to reduce the bioavailability of contaminants, and consequently decrease their accumulation and toxicity in plant and animals.

Biochar is emerging as an ameliorant to reduce the bioavailability of contaminants in the environment with additional benefits of soil fertilization and mitigation of climate change (Sohi, 2012).

2. Biochar for remediation of toxic metals in soils

Beesley et al. (2010) applied a hardwood-derived biochar to multi-metals (arsenic [As], copper
[Cu], cadmium [Cd], and zinc [Zn]) contaminated soil. Interestingly, Cu and As were mobilized, whereas Cd and Zn are immobilized in soils amended with biochar as compared to un-amended soil. Copper leaching was associated with high dissolved organic C contents at the increased pH induced by applying biochar, whereas As leaching was attributed to increasing the soil pH to 7.56 (Almaroai et al., 2014).

Similarly, Park et al. (2011a) reported Cu mobility in soil due to increased dissolved organic C with the addition of a chicken manure-derived biochar. In contrast, the high pH induced by biochar results in reduced solubility of Cd and Zn (Ahmad et al., 2012a; 2012b; 2012c; 2012d).

Increased mobility of As with biochar in soil was also reported by Hartley et al. (2009), and has been attributed to the rise in soil pH as well as As competition with soluble P in biochar. Biochar can also reduce As(V) to As(III), thereby enhancing As mobility (Ahmad et al., 2014a; Almaroai et al., 2012; 2013a; Lim et al., 2014; Park et al., 2011b; Zhang et al., 2013).

Interestingly, reduced As availability has observed by Ahamd et al. (Fig. 1, unpublished data) in contaminated soils amended with pine needles-derived biochars pyrolyzed at 300 and 700°C. Hence, the type of feed stocks could be a determinant factor on soil As mobility.

![Fig. 1](image-url) Exchangeable (a) lead (Pb) and (b) arsenic (As), and TCLP (c) Pb and (d) As in soils treated with soybean stover biomass (S-BM), soybean stover-derived biochars pyrolyzed at 300°C (S-BC300) and 700°C (S-BC700), pine needles biomass (P-BM), and pine needles-derived biochars pyrolyzed at 300°C (P-BC300) and 700°C (P-BC700). Asterisk (*) shows concentration below detection limit (0.01 mg L⁻¹). Bars with the same letters above are not different at a 0.05 significance level (Ahamd et al. unpublished data)

Firing range soil treated with biochar showed reduced Pb mobility and enhanced antimony [Sb] mobility (Fig. 2) (Ahmad et al., 2012d; 2012e; 2014b; Hashimoto et al., 2013; Lee et al., 2013a; 2013b; Zhao et al., 2013). Oxyanion, Sb, also shows higher mobility in a soil treated with a broiler litter-derived biochar (Uchimiya et al., 2012). The electrostatic repulsion between anionic Sb and
negatively charged biochar surfaces could have resulted in desorption of Sb. Conversely, the electrostatic attraction between positively charged Cu and negatively charged biochar is the prevailing mechanism of Cu immobilization in San Joaquin soil (Uchimiya et al., 2011b). Notably, Cu mobility/immobility is highly influenced by biochar organic C content (Awad et al., 2012; 2013; Moon et al., 2011; 2013). Generally, the biochars produced at <500 °C have high dissolved organic C content, which could facilitate the formation of soluble Cu complexes with dissolved organic C, as reported by Beesley et al. (2010) and Park et al. (2011a). Additionally, dissolved organic C can block the pores of biochars preventing Cu sorption (Cao et al., 2011). However, the biochars produced at high temperatures (>600 °C) are generally deficient in dissolved organic C, which could affect Cu immobility in soil, as reported by Uchimiya et al. (2011a; 2011b).

Fig. 2. Exchangeable (a) lead (Pb) and (b) antimony (Sb) concentrations in firing range soils treated with mussel shell powder (MS), cow bone powder (CB) or biochar (BC). The same letters above each bar indicate no difference between treatments at a 0.05 significance level (adapted from Ahmad et al., 2014a).
The effect of pyrolysis temperature on the retention of Pb by broiler litter-derived biochars produced at 350 and 650°C was recently evaluated by Uchimiya et al. (2012). Those authors reported that biochar produced at a low pyrolysis temperature is favorable for immobilizing Pb. The increased release of available P, K, and Ca from biochars produced at a low temperature is associated with high Pb stabilization (Mohan et al., 2014).

Cao et al. (2011) demonstrated by X-ray diffraction (XRD) analysis that biochar derived from dairy manure containing a high amount of available P immobilized Pb in shooting range soil by forming insoluble hydroxypyromorphite (Pb₅(PO₄)₃(OH)).

The role of O-containing functional groups on biochar surfaces towards metal binding was predicted by Uchimiya et al. (2011b), who reported that cottonseed hull-derived biochar produced at 350°C contains high O content resulting in high uptake of Cu, nickel [Ni], Cd, and Pb.

Soil pH is considered to greatly influence the mobility of metals. Generally biochar is alkaline, thereby inducing a liming effect in soil and causes immobilization of metals and mobilization of oxyanions (Almaroai et al., 2013a; 2013b; 2014; Ok et al., 2007; Saifullah et al., 2014; Usman et al., 2012; 2013).

As discussed earlier, biochar-induced increases in soil pH can also influence the sorption of metals. For instance, Ahmad et al. (2013) reported that in soil amended with biochar, rise in soil pH favored the sorption of Pb onto kaolinite making charge on kaolinite more negative. At pH > 5, Pb forms strong inner sphere bidentate surface complexes with kaolinite (Gräfe et al., 2007).

Biochar shows the potential to mitigate Cr contaminated soils as they are highly reactive with many functional groups and are able to donate electrons (Choppala et al., 2012). The increase in proton supply for Cr(VI) reduction may be attributed to the presence of several O-containing acidic (carbonyl, lactonic, carboxylic, hydroxyl, and phenol) and basic (chromene, ketone, and pyrone) functional groups (Boehm, 1994; Goldberg, 1985). The resulting Cr(III) either adsorbs or participates in surface complexation with organic amendments. However, high pH biochars may prevent dissociation and oxidation of phenolic and hydroxy groups, which may limit the supply of protons for reducing Cr(VI) (Choppala et al., 2012). Moreover, soil microbes can also cause the reduction of Cr(VI) to Cr(III) using C as an energy source from the biochar (Zimmerman, 2010). Because of the lower solubility of Cr(III) than Cr(VI), this reduction eventually results in immobilizing the Cr, thereby diminishing mobility and transport (Choppala et al., 2012).

Ion-exchange, electrostatic attraction and precipitation are prevailing mechanisms for the remediation of inorganic contaminants by biochar (Fig. 3).
3. Rice paddy soils

Heavy metal contamination in paddy soils is one of the most serious issues confronting rice production and soil management in Asian countries. Especially in Korea, the large paddy areas have been severely contaminated by Cd and Pb via effluent from mine tailings and other wastes generated by closed or abandoned mines (Ok et al., 2010; 2011a; 2011b; 2011c). As a result, accumulation of heavy metals into rice plants has produced a major environmental risk to human health (Vithanage et al., 2014; Yang et al., 2007; 2008).

Biochar showed a vital contribution to reduce the Cd and Pb bioavailability in contaminated paddy soils, while reducing the pant uptake and grain accumulation. A three years experiment conducted at a contaminated rice paddy in southern China single amended with wheat straw biochar showed a reduction of soil extractable Cd and Pb. Moreover, rice plant tissues’ Cd content was significantly reduced, depending on the biochar application rate. Root tissue Pb content also was found to decrease. Cd and Pb bonded with the aluminum (Al), iron (Fe) and phosphorus (P) on and around and inside of the biochar particles. Cation exchange sites on the porous carbon structure can also be a possible reason for the Pb and Cd immobilization in the contaminated paddy soil (Bian et al., 2014a). Similarly, Municipal biowaste biochar decreased the soil availability of Cd and grain Cd content during both rice
and wheat seasons in a rice paddy soil in eastern China (Bian et al., 2014b). Biochar soil amendment in a contaminated rice paddy in southern China was reduced rice grain Cd content by 20-90% (Bian et al., 2013). Reduced Cd bioavailability in soil and wheat grain Cd content following to the biochar application in a contaminated paddy soil have been also reported by Cui et al. (2012). In all these studies pH increment with biochar amendment was the critical reason for low Cd bioavailability and reduced plant uptake.

Interestingly, Cui et al. (2012) reported rice plant Cd uptake reduction in contaminated rice paddy in the second year compared to in the first year regardless to a single application of biochar as a basal in the first year. Hence, long term effect of biochar has profound its implication in contaminated paddy soils as a better bio-resource.

4. Smart biochar

Biochar surface modification or smart biochar production is concerned by scientists to improve the biochar qualities to use them in different areas (Sohi, 2012). Recently, the concept of engineered biochar has been used to various biochar composites for CO₂ sorption and environmental remediation (Yao et al., 2013; Zhang et al., 2012).

Biochar revealed promising results in toxic heavy metal remediation in contaminated soils. As explained above, biochar may increase the bioavailability of As, Cu and Sb. Hence, application of biochar for multi-metals contaminated soils may cause unexpected environmental problems. Song et al. (2014) used MnOₓ for biochar surface modification and it was demonstrated increased Cu²⁺ adsorption to the biochar surface. This enhanced Cu²⁺ adsorption was mainly due to the formation of inner-sphere complexes with MnOₓ and O containing groups on biochar surface. The stronger binding affinity of Cu²⁺ with MnOₓ-loaded biochar was also helped for lower desorption rate relative to unmodified biochar. Surface modified biochar with Al(III) also showed better As(V) sorption under acidic condition than the unmodified biochar (Qian et al., 2013).

Smart biochar in metal remediation is still not employed well. Hence, smart biochar technology needs to be tested and used in metal remediation. It would be a possible scenario to remediate all types of metals in contaminated soils.

5. Conclusions

In recent years, biochar has been proposed as means of restoring or sequestering C within soil. The proposed benefits of biochar applications include the decreases of greenhouse gas (GHG) emissions, increases of nutrient and water retention of soils, stabilization of native soil organic matter, and decreases of the bioavailability of contaminants in soils. Biochar-induced immobilization of toxic metals in contaminated soils has recently received considerable attention. Despite the apparent benefits of biochar towards a variety of soil parameters, a fundamental knowledge of metal-biochar interactions is still lacking.

All biochars are not equally effective for immobilizing metals in soils. Therefore, the development and selection of proper biochars is very important prior to its application on the large-scale contaminated sites. Research on biochar is contemporary and still needs in-depth investigations to determine the long-term effects of biochar.

6. Acknowledgement

Significant part of the manuscript is based on author’s previous publications (Chemosphere 99:19-33). This study was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science and Technology (2012R1A1B3001409).
7. References


Monitoring of Radiocesium contamination in farmland soil in eastern Japan
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Abstract:

Key Words: radiocesium, Fukushima Dai-ichi Nuclear Power Plant, soil contamination, concentration map, air dose rate

1. Introduction

Radionuclides released to the environment by the accident at the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) operated by the Tokyo Electric Power Company, struck by the Great East Japan Earthquake and subsequent tsunami on March 11, 2011. Radionuclides were transported and deposited in large area of terrestrial and marine environments.

As a result, radioactive materials were detected in drinking water, agricultural products such as vegetables, milk, tea leaves, and so on. In early stage of environmental contamination, the main radionuclide for contamination was $^{131}$I and it changed to $^{134}$Cs and $^{137}$Cs. It is known that such a contamination occurred in the Chernobyl Nuclear Power Plant accident in 1986 and has continued for a long time. Concerning monitoring of environmental radionuclides, National Institute for Agro-Environmental Sciences (NIAES) has been monitoring concentration $^{137}$Cs and $^{90}$Sr in soil, rice and wheat since 1959 (Komamura et al., 2005, 2006). After the FDNPP accident, NIAES worked on measurement of concentration of $^{131}$I, $^{134}$Cs and $^{137}$Cs in agricultural products and soil, investigation of radionuclides contamination status in farmland, development of remediation method, etc. to provide important information to the Ministry of Agriculture, Forestry and Fisheries (MAFF).

In this paper, the authors introduce the research activities in NIAES, especially focusing the monitoring of radiocesium contamination in farmland soil in Fukushima prefecture and its surround region.

1-1 Research activities in NIAES

1-1-1 Long term monitoring of radioactive contamination in rice, wheat and soil

The concentrations of $^{90}$Sr, $^{137}$Cs in rice (unpolished and polished), wheat (grain and flour) and soil (same field as rice or wheat cultivated) of 17 agricultural fields were measured since 1959 to monitor influence of radioactive fallout (Fig. 1) (Komamura et al. 2005). It was found that the largest annual precipitation of radioactive fallout was observed in 1963 and that the concentrations of $^{90}$Sr and
137Cs in rice, wheat, and soils gradually declined after 1966. At the Chernobyl accident, the contamination of rice and soil was not obvious. On the other hand, an increased concentration of 137Cs was found in some wheat grains that had been contaminated by fallout at the heading time of wheat. Based on long-term monitoring, residence half-life of 137Cs in paddy plow layer and upland plow layer was estimated to be 9-24 and 8-26 years, respectively (Komamura et al. 2006). Moreover, transfer factor of 137Cs from soil to polished rice was determined as $2.6 \times 10^{-3}$ (Komamura et al. 1994).

1-1-2 NIAES research works after the accident

In NIAES, temporal change of air dose rate and radionuclides concentration in leaf vegetables cultivated in monitoring field was measured just after the accident. These information were provided to the MAFF to determine various countermeasures. We also worked on measurement of agricultural products, investigation of radionuclides concentration in farmland soil and method of decontamination in 2011. High concentration of agricultural products were found in several places in 2011 crop season. Therefore, reducing crop contamination, radiocesium fixation by soil and radiocesium dynamics in agro-environment became new themes in 2012. Yamaguchi et al. (2012) reviewed the behavior of radiocesium in soil-plant systems and its controlling factor. This review article helped many researchers in agronomy sector because they did not have enough knowledge about radioactive materials.

1-2 Monitoring survey for air dose ratio and concentration of radioactive materials in soil in the early stage of the accident

1-2-1 Air dose rate monitoring in Fukushima prefecture

After the accident, deposition of radionuclides and air dose rate was measured FDNPP surround area. Soil concentration of radionuclides such as 131I, 134Cs, 137Cs, etc. were measured in about 100 sites. The number of sites were limited because measurement took a long time. On the contrary, air dose rate was measured at many points such as playgrounds and public facilities because it indicated influence of human health by radioactivity and it could be measured easier than soil concentration. In Fukushima prefecture, air dose rate at about 1600 schools were measured in from April 5 to 7, 2011 (Fukushima prefecture 2011a). Grid survey of air dose rate at about 1,900 points was also carried out (Fukushima prefecture 2011b). These results were the effective information for spatial distribution of air dose rate.

The exclusion zone where distance from FDNPP was within 20 km and the evacuation-prepared area in case of emergency where distance from FDNPP was within ca 30 km was set immediately after the accident. The deliberate evacuation area where air dose rate showed very high was added in April 2011. These areas were called “evacuation zone” (Fig. 2). The evacuation zone was revised as areas where residents have difficulties in returning for a long time, areas in which the residents are not permitted to live, and areas to which evacuation orders are ready to be lifted in October 2013.

In August 2011, the systematic survey to measure air dose rate and soil concentration of radioactive nuclides in the area where the distance was more than 20 km from FDNPP was carried out by the Ministry of Education, Culture, Sports, Science and Technology (MEXT). In the survey, air dose rate and deposition of 131I, 134Cs and 137Cs was measured.
in about 2200 points and distribution maps were created.

1-2-2 Survey for rice cultivation

After the accident, the urgent paddy soil survey was conducted to delineate suitable area for rice cropping from late March to early April in 2011 by the prefectural governments. Totally 242 paddy field in 9 prefectures of eastern Japan were investigated. The concentration of radiocesium (sum of $^{134}$Cs and $^{137}$Cs, radio-Cs concentration hereinafter) ranged from 9 to 29000 Bq/kg in Fukushima prefecture and from ND (below detection limit) to 1826 Bq/kg in the other prefectures (Miyagi prefecture 2011, Yamagata prefecture 2011, Fukushima Prefecture 2011c, Ibaraki prefecture 2011, Tochigi prefecture 2011, Gunma prefecture 2011, Chiba prefecture 2011, Kanagawa prefecture 2011). In this survey, only in the evacuation zone, radio-Cs concentration exceeded 5000 Bq/kg which was set as the upper limit concentration for rice cultivation (Fig. 3). As a result, rice was cultivated except the evacuation zone in 2011.

As the number of investigated sites were limited in this survey, it was required more detail survey and the distribution map of radionuclides concentration in farmland soil as a basic information for crop production, various countermeasures and decontamination. Therefore, we conducted investigation of farmland soil in a several times and monitored radio-Cs concentration of soil in Fukushima and neighbor prefectures.

2. Material and Method

2-1 Soil survey

The soil survey was conducted 4 times until FY2012; 2 times in FY2011 and 1 time in FY2012. The first soil survey was carried out at 355 sites of farmland in 6 prefectures from May to August in 2011. The second soil survey was carried out at 3423 sites of farmland in 15 prefectures from October 2011 to February 2012. The third soil survey was carried out at 446 sites of farmland in 6 prefectures from April 2012 to April 2013. This paper mainly focused the second soil survey because it covered the widest region and the sampling density was the highest among 3 surveys. In each soil survey, the sampling sites were selected in paddy, upland, orchard and grassland which
was innovated after April 2011. Soil samples were collected at 5 points in each site using soil sampler (50 mm diameter and 30 cm depth with inner PVC tube) (Figs. 4 and 5). At the same time air dose rate at 1 m height was measured using NaI or CsI scintillation survey meter and geographic position was determined using GPS equipment. Some field information such as crop, plowing after the accident and status of soil surface cover at the accident were investigated.

2-2 Soil analysis

Five samples at each site were mixed after divided into depth of 0-15 cm, 15-20 cm, 20-25 cm and 25-30 cm. The concentration of $^{131}$I was already less than detection limit in almost all sites in May 2011 because of its short half-life; 7 days. Therefore, concentration of $^{134}$Cs and $^{137}$Cs of 0-15 cm depth soil samples were measured using germanium semiconductor detectors (Observation and Safety section, Ministry of Health, Labour and Welfare 2002). Measurement time was 1000 – 10000 seconds. The concentration was indicated as Bq/kg dry soil at both sampling day and base day in each survey. The base day of first, second and third survey was June 14, 2011, November 5, 2011 and December 28, 2012, respectively.

2-3 Estimation method of radiocesium concentration and making map

The relationship between air dose rate and radio-Cs concentration was analyzed. For this analysis, soil type, land use and plowing after the accidents were considered.

As the map of air dose rate by airborne survey was prepared by MEXT, Ministry of Education, Culture, Sports, Science and Technology (MEXT 2011), we used this map for spatial distribution of air dose rate. Adding to it, the soil map of farmland (Takata et al. 2011) was also used. The kriging method was applied to improve accuracy of the estimated map. For geographic analysis and mapping, GIS software (ArcView ver 10 and spatial analyst; ESRI) was used. The detail of procedure was described by Takata et al. (2014).

3. Results and discussion

3-1 Concentration of radiocesium in soil

Radiocesium was detected in Tohoku and Kanto region in second soil survey (Table 1). In Fukushima prefecture, radio-Cs concentration in 188 sites exceeded 5000 Bq/kg and most of sites (179

<table>
<thead>
<tr>
<th>Prefecture</th>
<th>Total</th>
<th>Paddy</th>
<th>Upland</th>
<th>Meadow</th>
<th>Orchard</th>
<th>Radio-Cs concentration *1, 2</th>
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<td>2030</td>
<td>1062</td>
<td>107</td>
<td>224</td>
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</table>

*1 Radio-Cs concentrations are corrected at December 28, 2012
*2 Radio-Cs concentration less than detection limit are described as “<” + detection limit.
sites) were located inside of evacuation zone. It was considered that the distribution of radionuclides was strongly affected by the wind and precipitation at the accident. As a result, evacuation zone (mainly northwest direction from FDNPP) showed high concentration, followed by the central part of Fukushima prefecture (area of along the River Abukuma) and northeastern part of Tochigi prefecture. The highest radio-Cs concentration (203095 Bq/kg) was observed in Ohkuma Town, which is located on approximately 3 km southwest of FDNPP.

3-2 Relationship between soil radiocesium concentration and air dose rate

The relationship between radio-Cs concentration in soil and air dose rate at 1 m height is shown in Fig. 6a. Air dose rate data at the sites covered with snow or water (from precipitation) were excluded from this analysis, because radiation from the soil surface is blocked by snow and water. Data with concentration of $^{134}\text{Cs}$ or $^{137}\text{Cs}$ below the detection limit were also excluded from the analysis. Though a linear relationship was shown between radio-Cs concentration in soil and air dose rate, this relationship was affected by soil surface condition, soil group and land use type. Plowed fields (paddy and upland) showed a gentler slope of the regression line than did unplowed fields (Fig. 6b). It is well known that plowing dilutes the radionuclides in the plowed layer by mixing the contaminated surface layer with non-contaminated subsurface layers, thereby reducing the air dose rate (Alexakhin 1993; Vovk et al. 1993; EURANOS 2010). Slope of the regression line in non-Andosols group was slightly smaller than that in Andosols group, which was characterized by low bulk density (Nanzyo et al. 1993) (Fig. 6c). This difference in slope between Andosols and non-Andosols could result from the difference in bulk density. Furthermore, paddy fields showed slightly gentler slopes than did upland fields (Fig. 6d). In general, the plowed layer is shallower in paddy fields than in upland fields, which might influence the regression slope.

Fig. 6 Relationship between radio-Cs concentration and air dose rate; (a) whole dataset, (b) divided into plowed or non-plowed, (c) divided into Andosols or non-Andosols and (d) divided into paddy fields or upland fields. (Takata et al. 2014)
Table 2 Regression results for predicting radio-Cs concentration (SoilCs) using air dose rate (D.R.)

(Takata et al. 2014)

<table>
<thead>
<tr>
<th>Area</th>
<th>Equation #</th>
<th>Land use</th>
<th>Soil group</th>
<th>Equation</th>
<th>R²</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evacuation-directive</td>
<td>Reg. 1</td>
<td>Paddy field, upland fields</td>
<td>Andosols</td>
<td>D. R. = 2.88 x 10^{-4} x SoilCs</td>
<td>0.89</td>
<td>99</td>
</tr>
<tr>
<td>Zone (Non-ploughing)</td>
<td>Reg. 2</td>
<td>Paddy field, upland fields</td>
<td>Non-Andosols</td>
<td>D. R. = 4.33 x 10^{-4} x SoilCs</td>
<td>0.90</td>
<td>435</td>
</tr>
<tr>
<td>Zone (Non-ploughing)</td>
<td>Reg. 3</td>
<td>Orchard</td>
<td></td>
<td>D. R. = 3.96 x 10^{-4} x SoilCs</td>
<td>0.99</td>
<td>14</td>
</tr>
<tr>
<td>Zone (Non-ploughing)</td>
<td>Reg. 4</td>
<td>Meadow</td>
<td></td>
<td>D. R. = 5.99 x 10^{-4} x SoilCs</td>
<td>0.90</td>
<td>27</td>
</tr>
<tr>
<td>Non-Evacuation Zone</td>
<td>Reg. 5</td>
<td>Paddy field</td>
<td>Andosols</td>
<td>D. R. = 3.30 x 10^{-4} x SoilCs + 0.050</td>
<td>0.83</td>
<td>264</td>
</tr>
<tr>
<td>Zone (Non-ploughing)</td>
<td>Reg. 6</td>
<td>Paddy field</td>
<td>Non-Andosols</td>
<td>D. R. = 3.79 x 10^{-4} x SoilCs + 0.027</td>
<td>0.78</td>
<td>630</td>
</tr>
<tr>
<td>Zone (Non-ploughing)</td>
<td>Reg. 7</td>
<td>Upland field</td>
<td>Andosols</td>
<td>D. R. = 3.88 x 10^{-4} x SoilCs + 0.015</td>
<td>0.78</td>
<td>219</td>
</tr>
<tr>
<td>Zone (Non-ploughing)</td>
<td>Reg. 8</td>
<td>Upland field</td>
<td>Non-Andosols</td>
<td>D. R. = 4.04 x 10^{-4} x SoilCs + 0.023</td>
<td>0.79</td>
<td>330</td>
</tr>
<tr>
<td>Zone (Non-ploughing)</td>
<td>Reg. 9</td>
<td>Orchard</td>
<td></td>
<td>D. R. = 6.19 x 10^{-4} x SoilCs</td>
<td>0.54</td>
<td>161</td>
</tr>
<tr>
<td>Zone (Non-ploughing)</td>
<td>Reg. 10</td>
<td>Meadow</td>
<td></td>
<td>D. R. = 9.46 x 10^{-4} x SoilCs</td>
<td>0.40</td>
<td>24</td>
</tr>
</tbody>
</table>

*1: equivalent dose rate (µSv h⁻¹) at 1 m height; *2: soil Cs concentration (Bq kg⁻¹).

Fig. 7 Flowchart of the spatial prediction of radio-Cs concentration; (a) 10 regression equations, (b) air dose rate map prepared by MEXT, (c) cultivated soil-land use map, (d) radio-Cs concentration map created from regression models, (e) distribution pattern of the regression residual. (Takata et al. 2014)
Therefore, we conducted regression analysis with 10 groups (Table 2). The coefficients of determination ($R^2$) were within the range 0.40–0.99, and they were higher in the evacuation zone than in the non-evacuation zone. There were intact land surface conditions in non-plowed fields, which might have resulted in the strong relationship between radio-Cs concentration in soil and the air dose rate in the evacuation zone. Orchards and meadows in the non-evacuation zone showed a relatively weak relationship between radio-Cs concentration and air dose rate.

3-3 Distribution map of radiocesium concentration in farmland soil

To delineate areas above mentioned 10 groups, the cultivated soil land use map (Takata et al. 2011), the actual distribution map of paddy fields in the 2011 season that was constructed by remote sensing, evacuation zone map were used (Fig. 7a–c). Ten regression equations (Table 2) and the air dose rate map prepared by MEXT were used to construct 10 group maps of radio-Ce concentration in soil. These maps were combined and map of radio-Cs concentration in soil was created (Fig. 7d). Then, the residue of the estimated radio-Cs concentration in soil was calculated using actual data and estimated data. According to residue map (Fig. 7e), spatial bias was found in some areas. It might be caused by difference in scintillation survey meter used for field measurement, in the period of the aerial monitoring, in topographical location and so on. We improved the estimated map by adopting regression-kriging (RK) model (Fig. 8). As a result, RMSE and ME of the RK model were 760 and –100, and these were slightly lower than those of the regression model (RMSE = 790, ME = –220). This result indicated that the RK model gave higher prediction accuracy and lower prediction bias than in the regression model.

3-4 Area of contaminated farmland

MAFF has issued guidance for decontamination of radiocesium in farmland (MAFF 2012), and several countermeasures based on the radio-Cs concentration level are summarized in Table 3.
According to this, farmland of radio-Cs concentration exceeding 5000 Bq/kg is required to remove surface soil. We calculated the area of contaminated farmland based on the concentration level from the map (Table 4). Farmland exceeding 5000 Bq/kg was estimated 8900 ha (5900 ha in paddy and 3000 ha in upland) and most of the farmland located inside of evacuation zone.

### 3-5 Use of radio-Cs concentration map

The radio-Cs concentration of brown rice harvested in 2011 was investigated in eastern Japan and some

---

Table 3 Guideline for soil decontamination technique (MAFF 2012)

<table>
<thead>
<tr>
<th>Contamination level</th>
<th>Recommendable technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 5000 Bq/kg</td>
<td>(1) Topsoil removal if field did not plowed.</td>
</tr>
<tr>
<td></td>
<td>(2) Soil turning tillage</td>
</tr>
<tr>
<td></td>
<td>(3) Management to reduce radionuclide uptake by crops</td>
</tr>
<tr>
<td></td>
<td>(4) Soil mixing by water and suspension removal if enough water is available</td>
</tr>
<tr>
<td>Paddy field</td>
<td>Upland field</td>
</tr>
<tr>
<td>Lowland soil</td>
<td>Other soils</td>
</tr>
<tr>
<td>Groundwater level is low</td>
<td>Groundwater level is high</td>
</tr>
<tr>
<td>5000 – 10000 Bq/kg</td>
<td>(1) Topsoil removal (2) Soil mixing by water and suspension removal</td>
</tr>
<tr>
<td></td>
<td>(3) Soil turning tillage, if groundwater level is low</td>
</tr>
<tr>
<td>10000 – 25000 Bq/kg</td>
<td>(1) Topsoil removal</td>
</tr>
<tr>
<td>25000 Bq/kg or more</td>
<td>(1) Topsoil removal measures to prevent soil scattering is required (Fixation agent, etc)</td>
</tr>
</tbody>
</table>

Table 4 Estimated area by radio-Cs concentration level (Kohyama et al. 2014)

<table>
<thead>
<tr>
<th>Paddy field</th>
<th>Upland field, Orchard and Meadow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bq/kg</td>
<td>0-500</td>
</tr>
<tr>
<td>ha</td>
<td>0-500</td>
</tr>
<tr>
<td>Iwate</td>
<td>94700</td>
</tr>
<tr>
<td>Miyagi</td>
<td>103700</td>
</tr>
<tr>
<td>Yamagata</td>
<td>96700</td>
</tr>
<tr>
<td>Fukushima</td>
<td>47300</td>
</tr>
<tr>
<td>(EE)*</td>
<td>–</td>
</tr>
<tr>
<td>(DEA)*</td>
<td>–</td>
</tr>
<tr>
<td>(EPAE)*</td>
<td>–</td>
</tr>
<tr>
<td>Ibaraki</td>
<td>94900</td>
</tr>
<tr>
<td>Tochigi</td>
<td>81900</td>
</tr>
<tr>
<td>Gunma</td>
<td>26200</td>
</tr>
<tr>
<td>Saitama</td>
<td>44000</td>
</tr>
<tr>
<td>Chiba</td>
<td>73200</td>
</tr>
<tr>
<td>Tokyo</td>
<td>300</td>
</tr>
<tr>
<td>Kamagawa</td>
<td>400</td>
</tr>
<tr>
<td>Niigata</td>
<td>154400</td>
</tr>
<tr>
<td>Yamanashi</td>
<td>830</td>
</tr>
<tr>
<td>Nagano</td>
<td>55400</td>
</tr>
<tr>
<td>Shizuoka</td>
<td>23200</td>
</tr>
</tbody>
</table>

Values of area are rounded.
rice were detected radiocesium more than detection limit; 20 Bq/kg. In Fukushima prefecture, brown rice exceeding 500 Bq/kg were found. Though the high concentration rice were found in the area where radio-Cs concentration of soil was high, the relationship between radio-Cs concentration of soil and brown rice was not clear (Fig 9). According to the result of cause analysis, not only the concentration of soil but also soil properties, amount of fertilizer application, management, etc. influenced the high radio-Cs concentration of brown rice (Fukushima prefecture and MAFF 2012).

Soil properties which influence the radiocesium uptake by crop were investigated (MAFF 2013). The result showed that exchangeable radiocesium, exchangeable potassium and RIP (Radiocesium Interception Potential) were important factors. The risk evaluation to radiocesium is required to reduce radiocesium contamination of agricultural products. The radio-Cs concentration map becomes an important information for the spatial risk evaluation.

4. Conclusion

In this study, we created radio-Cs concentration map in farmland soil of eastern Japan. Areas of farmland exceeding 5000 Bq/kg covered about 5900 ha of paddy fields and 3000 ha of upland fields in Fukushima Prefecture, and were distributed mainly in the evacuation zone. The map was used for basic information to determine appropriate technology for decontamination and for reducing crop contamination. We should continue monitoring status of Cs contamination to produce safe foods.

5. Acknowledgements

We thank the staff of the agriculture departments of 15 prefectures (Fukushima, Iwate, Miyagi, Yamagata, Ibaraki, Tochigi, Gunma, Saitama, Chiba, Tokyo, Kanagawa, Yamanashi, Nagano, Shizuoka and Niigata) for collection data. This work was supported by the 2011 radioactive measurement and investigation project entitled “Study on change in distribution of radioactive substances in farmland” which was founded by the Ministry of Agriculture, Forestry and Fisheries. Radioactive Cs concentration in soil was measured by Hitachi Kyowa Engineering Co., Ltd. and the Kyushu Environmental Evaluation Association.

6. References

Mitigation of Radioactive Contamination from Farmland Environment and Agricultural Products

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Abstract: Radioactive Cs contamination of vast area including crop land with a focus on TEPCO’s Fukushima Daiichi Nuclear Power Plant accident in March 2011, still ask farmers to reduce the uptake of radioactive materials to the crops in the farmland even today a lapse of three years. Several removal technologies from the paddy and upland soils, volume reduction of waste materials, and potassium fertilizer application to reduce the uptake of radioactive cesium (Cs) to the edible part of plant will be presented. In the case of food supply, as the concentration of radioactive substances in food less than standard value (100 Bq/kg) is required, sufficient removal of radioactive Cs from the field and reduction of transfer factor from soil to plant by maintaining potassium levels in soil throughout the growth stage, successively reduced the number of food samples with excess levels of radioactive Cs in food products. Furthermore, the food processing steps also played an important role to remove the radioactive Cs from the food (such as wheat, soybean, etc.). On the other hand, attention should be paid to reduction of radiation exposure of farm workers during their labor in the fields, by removing or shielding the radioactive Cs from the environment. Several agricultural machineries have been modified to adapt in contaminated areas. As the contaminated soil is limited to the very thin but fertile top soil layer, removal of contaminated soil and top-dressing of non-contaminated but low fertile soil sometimes reduce the fertility of the field and also induce erosion, so we also attempt to develop methods to compensate the productivity after the decontamination of the field by applying forage grasses to increase the soil fertility and reduce the possible erosion of topsoil from the field.

Key Words: Decontamination, Radioactive Cs, Transfer factor of Cs, Volume reduction of waste

1. Introduction

A large area of Eastern Japan was contaminated by radioactive Cesium ($^{134}$Cs and $^{137}$Cs) because of the explosion of Fukushima Daiichi Nuclear Power Station (FDNPP) after the attack of Great East Japan Earthquake occurred in 11$^{th}$ March 2011 (Fig. 1). Not only Fukushima prefecture, those adjacent prefectures were also suffered by radioactive Cs to some extent.

Fig. 1 Airborne monitoring survey of soil surface radioactive Cs (sum of $^{134}$Cs and $^{137}$Cs, October 12, 2011) (MEXT 2011)

Table 1 indicates the top 12 prefectures of agricultural working population and agricultural production in 2010 among 47 prefectures in Japan. It indicates that those prefectures played important roles in Japanese agricultural activity. As shown in Fig. 1, the contamination by radioactive Cs was mainly spread to the southern direction of Fukushima prefecture. This pattern is also observed in the report of contaminated agricultural products in 2011 (Fig. 2). In 2011, tea production was severely damaged as shown in Fig. 2. And the significant contamination was reported from as far as Shizuoka prefecture, which is about 400km from the FDNPP. It is important to consider the situation of vegetation at the time of the radioactive Cs scattering to the air. Though early March is just before the spring in these areas, while as tea plant is evergreen plant
species, the canopy was covered with leaves. Thus it is considered that the radioactive Cs was attached to the existing leaves on the top of the canopy. Distribution of radioactive Cs was investigated by dividing plant canopy into several parts as shown in Fig. 3, and it is confirmed that tea canopy trapped the radioactive Cs from the air. Furthermore, as there is a possibility that newly dressed radioactive Cs to the soil was absorbed by plant, then transported to the newly born tea leaves, stable Cs isotope was applied to soil or existing leaves, then the transportation to the newly born leaves was investigated (Fig. 4, Nonaka and Hirono 2011). It is demonstrated that the translocation from soil is negligible but those stable Cs applied to the existing leaves translocated to newly born leaves. Based on these observations, cutting off the leaves and branches at the top canopy is adopted. This countermeasure was effectively worked to reduce the contamination of tea plant, and further report of exceeding the limit value was not found after 2012. In the case of fruit trees, as most of them were deciduous trees, there was no green leaves at the timing of the event. Thus, direct attachment of radionuclides occurred on the surface of branch and trunk, and within the bark of tree. To remove the radioactive Cs from the fruit tree (e.g. Pair, peach, grape, persimmon, etc.), bark scraping by hand or high pressure washer was performed. This method effectively decreased the surface dose rate of tree (data not shown).

Table 1 List of agricultural working population and production (JPY) in top 12 prefectures in Japan (2010).

<table>
<thead>
<tr>
<th>Rank</th>
<th>Prefecture</th>
<th>Population (JPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ibaraki</td>
<td>113,287</td>
</tr>
<tr>
<td>2</td>
<td>Hokkaido</td>
<td>111,324</td>
</tr>
<tr>
<td>3</td>
<td>Chiba</td>
<td>109,048</td>
</tr>
<tr>
<td>4</td>
<td>Kagoshima</td>
<td>100,244</td>
</tr>
<tr>
<td>5</td>
<td>Kumamoto</td>
<td>98,988</td>
</tr>
<tr>
<td>6</td>
<td>Aichi</td>
<td>93,901</td>
</tr>
<tr>
<td>7</td>
<td>Iwate</td>
<td>89,993</td>
</tr>
<tr>
<td>8</td>
<td>Aomori</td>
<td>87,136</td>
</tr>
<tr>
<td>9</td>
<td>Niigata</td>
<td>80,483</td>
</tr>
<tr>
<td>10</td>
<td>Tochigi</td>
<td>79,881</td>
</tr>
<tr>
<td>11</td>
<td>Fukushima</td>
<td>77,359</td>
</tr>
<tr>
<td>12</td>
<td>Kagoshima</td>
<td>74,364</td>
</tr>
</tbody>
</table>

(Source: MAFF, Census of agriculture and forestry in Japan and MIC Statistics Bureau of Japan, Japan statistical yearbook)

Fig. 2 Agricultural products contamination by radioactive Cs reported in 2011 (Sum of $^{134}$Cs and $^{137}$Cs were higher than 100 Bq/kg FW).
(Source: MAFF, Results of inspections on radioactivity levels in agricultural products)
On the other hand, paddy fields and most of upland fields were not cultivated yet in early March, and most of the fallout was accumulated on the top of soil surface. Thus the decontamination of soil was required.

It is important to divide the strategy to decontaminate radioactive Cs from the soil from the viewpoint of agricultural products contamination and reduction of air dose level (Fig. 5). The purpose of the former target is to protect internal exposure by food intake of the consumers, and for this purpose the target level is put as 100 Bq/kg after 2012. And in this case, the condition of plow layer is focused and the detection is mainly operated by using Ge semiconductor detector. The latter target is to reduce external exposure of local residents, especially of farmers. For this purpose the target level is put not to exceed 1 mSv/year by the additional exposure by fallout. In this case, radioactive compounds located in the top soil layer is focused, thus surface soil layer is most important, and the detection was carried out mainly by survey meter.
To investigate and develop countermeasures on these topics, NARO put actual proof trials just after the event in 2011. The trials were carried out in Iitate village and adjacent Yamakiya district in Kawamata town (Fig. 6). The trial include top soil stripping, paddling and suspension removal, phytoremediation, and so on. Of course not all the trials finished successfully, we have concluded that the role of phytoremediation to remove radioactive Cs from soil is very limited (ca. 0.5% per one cultivation cycle), so we do not recommend phytoremediation for the effective method for decontamination of soil.

Fig. 5 Scheme of radioactive Cs removal from the soil.

Fig. 6 Actual proof trials in 2011.
It was concluded that physical removal of radioactive Cs from soil is most effective. However, we need to consider the decontamination technique based on two types of field condition, before tillage and after tillage (Fig. 7). If the soil was not disturbed by tillage, as radioactive cesium is limited in the top soil layer, most effective method is to remove top soil by stripping. This method is very effective but the problem is how to manage the disposal of soil after stripping. It is also possible to remove the top soil layer to the lower layer by inversion tillage. This technique also effectively to decrease the surface doses rate by the inhibition of radiation transmission by soil itself. And this technique is applied to those field whose surface radioactivity is not so high (that is, lower than 5,000 Bq/kg), and there is sufficient suitable deep soil layer also. Furthermore, if the soil contamination level is low, it is also possible to apply deep ploughing to dilute the radioactive materials in the soil. On the other hand, if the soil was cultivated before decontamination, top soil stripping is not applicable because huge amount of fertile soil is required to be removed. So, in the case of paddy field, paddling and suspension removal technique has been developed. This technique is based on the observation that most of the radioactive Cs is attached to the small soil particle mainly to the clay particle (Fig. 7).

Fig. 7 Decontamination of radioactive Cs from soil.

![Diagram of decontamination techniques](image)

![Pie chart of radioactive Cs distribution](chart)

Fig. 8 Distribution of radioactive Cs in clay, silt, fine sand and coarse sand (Left) and concentration of radioactive Cs in each fraction (Right). (source, MAFF 2013b)
Paddling and suspension technique is widely used paddy rice cultivation technique to prepare the soil suitable for transplanting of rice seedling (Fig. 9). Small soil particle containing clay fraction can be separated by applying this technique, radioactivity of the soil decreased effectively (data not shown).

Radioactive Cs distribution is not uniform and it is required to be monitored precisely. If the contamination level is high and required to treat not to disperse the soil during the decontamination, soil hardener technique is also proposed to fix the top soil (Fig. 10). Which make visible check of the target area and decrease the risk of soil particle intake by respiration who work there. Though the proposed technology and
corresponding contamination level is indicated in the Table, it should be decided based on each field condition and farmer’s request.

In 2011, though those areas which were suffered radioactive Cs fall out severely were prohibited to cultivate rice plant, rice cultivation was possible outside the prohibited area but some brown rice showed higher contamination level. To make clear the reason why high radioactive Cs concentration of brown rice occurred, produced rice and corresponding field soil data were collected and analyzed. At first the radioactive Cs concentration was plotted between soil and brown rice (Fig. 11). The relationship is not clear, and it is required to include another parameter to explain the result. It is reported that Cs uptake is mainly carried out by the activity of K transporter and the ratio of Cs to K concentration in the soil solution is important (Zhu and Smolder 2000). Thus K addition effectively decrease Cs uptake and transfer from soil to plant (Shaw and Bell 1991, Shaw et al. 1992, Zhu and Shaw 2000). When exchangeable K and transfer factor (TF) of rice in the corresponding field was plotted, there was a clear negative relationship (Fig. 12, NARO 2013). Which confirms that Cs uptake is also regulated by K transporter mediated pathway, thus the level of K in the soil is important. By using this result, if the soil radioactive cesium concentration is 5,000 Bq/kg, and the TF is 0.01 indicates that the radioactive Cs content in the rice would be 50 Bq/kg. So, it is proposed to keep the soil ex. K level to 25 mg K2O/100g throughout the growth. And this guideline was introduced for the rice production in 2012 and still in use.

Fig. 11 Relationship between radioactive Cs concentration of soil and brown rice grown in a same field.

Fig. 12 Relationship between soil exchangeable K and transfer factor. Transfer factor (TF) = Radioactive Cs in brown rice / Radioactive Cs in soil.
Based on these decontamination and mitigation efforts, the prohibition area for rice cultivation decreased year by year (Fig. 13). In 2011, the area was about 8,500ha, but in 2014, it was about 2,100ha.

The relationship between soil Exchangeable K and TF is also observed in field crops such as soybean and buckwheat (Fig. 14). Thus the Cs uptake from soil is dependent on the K status of the soil regardless of paddy or upland condition. Beside decontamination and mitigation of radioactive Cs, it is also important to address another aspect how to regulate the radioactive Cs contamination in the food. In Table 2, food processing factor using soybean is demonstrated. Food processing factor is designated as Food processing factor = Radioactive Cs content after processing (Bq/kg fresh weight) / Radioactive Cs content before processing (Bq/kg fresh weight). To make up the food stuff, we further process the material such as by

<table>
<thead>
<tr>
<th>Processed food stuff from soybean</th>
<th>Food processing factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tofu Soy pulp</td>
<td>0.18</td>
</tr>
<tr>
<td>Tofu Soy milk</td>
<td>0.13</td>
</tr>
<tr>
<td>Tofu Tofu</td>
<td>0.12</td>
</tr>
<tr>
<td>Natto Pressurized steam cooked beans</td>
<td>0.40</td>
</tr>
<tr>
<td>Natto Natto</td>
<td>0.40</td>
</tr>
<tr>
<td>Bold beans</td>
<td>0.20</td>
</tr>
</tbody>
</table>
adding water, boiling, fermentation. And final food radioactivity can be evaluated by using food processing factor as shown in Table 2. By using food processing factor, it is clearly shown that the level of radioactive Cs decreased by the food processing. And these results make the food manufacturer consider safer to use the agricultural products even under the limit value.

Though decontamination of the field by top soil stripping has been progressed to decrease the radioactivity, removal of contaminated soil can not be a simple answer. After top soil removal, soil is covered with additional soil as shown in Fig. 15. The required amount of additional soil is vast and they were taken from the surrounding mountainous area. The chemical properties of the additional soil is very poor (Table 3). Furthermore, decontamination by top soil stripping is preceded the initiation of agriculture, which means that even decontamination is finished, management of the field does not start immediately. Then weed invasion and erosion (especially in the upland field) are becoming another problem to be solved in these areas and cover crop introduction has been proposed and actual trial started.

![Fig. 15 Additional soil dressed after top soil stripping. (Iitate village, 2014)](image)

<table>
<thead>
<tr>
<th>Location</th>
<th>Sample number</th>
<th>Total N (%)</th>
<th>Humus content (%)</th>
<th>pH (H₂O)</th>
<th>Exchangeable K (K₂O mg/100g Soil)</th>
<th>Available P (P₂O₅ mg/100g Soil)</th>
<th>CEC (me/100g Soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iitate, Komiya</td>
<td>1</td>
<td>0.02</td>
<td>0.1</td>
<td>6.5</td>
<td>7</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Iitate, Komiya</td>
<td>2</td>
<td>0.03</td>
<td>0.5</td>
<td>6.4</td>
<td>5</td>
<td>15</td>
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<tr>
<td>Iitate, Komiya</td>
<td>3</td>
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<td>0.9</td>
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<td>8</td>
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<tr>
<td>Iitate, Kusano</td>
<td>4</td>
<td>0.01</td>
<td>0.2</td>
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<tr>
<td>Iitate, Kusano</td>
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<td>0.02</td>
<td>0.1</td>
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<tr>
<td>Iitate, Kusano</td>
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<td>0.02</td>
<td>0.4</td>
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<td>6</td>
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<tr>
<td>Iitate, Nagadoro</td>
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<td>5</td>
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</tr>
<tr>
<td>Iitate, Nagadoro</td>
<td>8</td>
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<td>0.2</td>
<td>6.5</td>
<td>5</td>
<td>18</td>
<td>5</td>
</tr>
</tbody>
</table>

Though applying decontamination and mitigation seems successfully improved the situation of food contamination and field radiation dose rate, the radioactive Cs contamination still trouble the farmers in the suffered area even after 3 and half years. To help them, we will further try to exclude the possibility of contamination of radioactive Cs from the environment to the food.

References
Development of Low-Cd Rice by mutation with Ion-beam

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Abstract: Rice (Oryza sativa L.) is a major dietary source of cadmium (Cd). However, there is currently no practical technique to substantially reduce Cd contamination of rice. Here, we report non-transgenic rice mutants from ion-beam irradiation that do not accumulate Cd in the grains and describe the mutant gene that is responsible. We found three mutants with low-Cd grains with different mutations of the same gene (OsNRAMP5). The defective transporter protein encoded by the mutant gene osnramp5 decreases root Cd influx. In Cd-contaminated paddy fields, the mutants have nearly undetectable Cd concentrations in their grains and exhibit no economically adverse traits. In addition, Cd and arsenic (As) levels in mutant simultaneously decreased under early-drainage conditions. DNA markers have been developed to facilitate marker-assisted selection of new cultivars carrying osnramp5. Our findings will help to greatly reduce Cd and As levels in paddy rice.

Key Words: Cadmium, ion-beam, arsenic, OsNramp5, rice

1. Introduction

Cadmium (Cd) is a contaminant that enters the food chain from multiple natural and industrial sources. Cd is toxic to the kidneys, and particularly to the proximal tubular cells, where it accumulates, leading to renal dysfunction (EFSA 2011). In Japan, itai-itai disease (renal osteomalacia), which is characterized by spinal and leg bone pain, is recognized as chronic toxicity induced by excess Cd in drinking water and crops (Tsuchiya 1976). To reduce the risk of Cd poisoning, the Joint FAO/WHO Expert Committee on Food Additives established a provisional tolerable monthly Cd intake of 25 µg kg⁻¹ body weight (FAO/WHO 2010), and the Codex Alimentarius Commission of the FAO/WHO established maximum Cd levels in food crops (Codex 2008). Among crops, the international criterion for rice Cd has been determined to be 0.4 mg kg⁻¹ polished rice; the value is two-fold higher than the criteria for other cereals such as wheat and maize and eight-fold higher than those for leaf vegetables. Rice is a staple food for nearly half of the world’s population, and global production and consumption of rice increased by approximately 300% from 1960 to 2011 (IRRI 2011). The demand for rice continues to grow, so it is necessary to produce low-Cd rice to reduce the potential risk that Cd poses to human health.

Cd uptake by paddy rice seems to be unique because it varies greatly depending on the soil redox potential in the paddy field. The bioavailable Cd in soil increases under oxidative conditions owing to the formation of soluble cadmium sulfate (CdSO₄) and decreases under reductive conditions because of the formation of less-soluble cadmium sulfide (CdS) (Arao et al. 2010). Therefore, unlike the upland crops, it is quite difficult to predict the rice grain Cd concentration from the soil Cd concentration and other soil chemical factors (Simmons et al. 2008). In addition, there are substantial genotypic differences in Cd accumulation in rice (Arao and Ishikawa 2006; Uraguchi et al. 2009). Generally, Cd concentrations are higher in indica-type varieties than in japonica-type ones. The genetic loci determining genotypic differences in Cd accumulation of rice have been shown by the QTL analysis for several mapping populations (Ishikawa et al. 2005; Ishikawa et al. 2010). Recently, the molecules involved in root Cd uptake (Nakanishi et al. 2006; Takahashi et al. 2011; Ishimaru et al. 2012), root vacuole sequestration of Cd (Ueno et al. 2010; Miyadate et al. 2011), root xylem loading of Cd (Satoh-Nagasawa et al. 2012), and phloem transport of Cd in the node (Uraguchi et al. 2011) have been successively found in rice, and therefore physiological and molecular processes of Cd transport in rice have been increasingly understood (Uraguchi and Fujiwara 2012). Although regulation of Cd transport by transgenic technique may enable us to reduce Cd accumulation in rice grains, commercial transgenic rice are not acceptable in Japan and many consumers fear eating the transgenic crops.

Mutations, induced by chemicals such as ethyl methane sulfonate (EMS) or ionizing radiation such as X-ray and gamma-ray, are a powerful way to explore novel mutants with the favorable traits in agriculture. Among mutagens, energetic heavy-ion beams have been recently used to generate such
mutants in higher plants because they are able to induce mutations with high frequency at a relative low dose at which virtually all plants survive, and they induce a broad spectrum of phenotypes without affecting other plant characteristics (Tanaka et al. 2010; Kazama et al. 2011). In addition, mutants produced by ion beam radiation are not transgenic plants, and are therefore more likely to be accepted by consumers, they are a practical choice for agriculture.

In the present study, we explored the rice mutants, produced by irradiation of heavy-ion beams, which are characterized by nearly non-detectable Cd in rice grain, even when cultivated in the paddy fields contaminated with high level of Cd. We also investigated the effectiveness of the low-Cd mutants to reduce simultaneously the levels of Cd and arsenic (As) in rice. Physiological, genetic, and molecular analyses were performed to identify a mutant gene responsible for low Cd in the rice mutants.

2. Materials and Methods

2.1. Production of rice mutants, growth conditions, and screening for low-Cd mutants

The husked seeds of rice (Oryza sativa L., cv. Koshihikari) were irradiated with 320 MeV carbon ions (\(^{12}\text{C}^{6+}\)) from an azimuthally varying field cyclotron (Japan Atomic Energy Agency, Takasaki, Gunma, Japan) at a dose of 40 Gy. Approximately 4000 M\(_1\) seeds were grown in a paddy field and self-pollinated, and the obtained seeds (M\(_2\)) were bulked. The 2,592 M\(_2\) seedlings produced from these seeds were transplanted into plastic pots filled with Cd-contaminated paddy soil (soil Cd concentration: 1.8 mg Cd kg\(^{-1}\)). We also grew 288 Koshihikari (wild-type, WT) seedlings in the soil. All M\(_2\) and WT plants were submerged until the booting stage, and then water was withheld to increase the bioavailable Cd concentration in the soil and enhance subsequent Cd uptake (Ishikawa et al. 2011). The grains were harvested from all plants and analyzed to determine their Cd concentrations, as described below.

To evaluate Cd uptake of the three candidate mutants (\(lcd-kmt1\), \(lcd-kmt2\), and \(lcd-kmt3\)) selected from 2,592 plants and the WT at the vegetative seedling stage, their M\(_3\) seedlings were exposed to 20 L of half-strength Kimura B solution (Ishikawa et al. 2011) with 0.18 µM CdSO\(_4\) added (pH 5.2) in a Biotron (NC350, NK System, Osaka, Japan). After 4 days, the plants were harvested for metal analysis.

2.2. Field experiments

The M\(_4\) plants of three mutants and the WT were cultivated in three Cd-polluted paddy fields in different regions of Japan. The soil Cd concentrations were 1.35 mg kg\(^{-1}\) (Field A), 1.21 mg kg\(^{-1}\) (Field B), and 0.35 mg kg\(^{-1}\) (Field C) when determined by 0.1 M HCl extraction. Seedlings were transplanted into the flooded paddy fields, with a single plant per hill, spaced at 15×30 cm and with 20 plants of each mutant and the WT per row, with each genotype planted in a separate row. After 1 month, the fields were managed by means of drainage and then intermittent irrigation until grain maturity. We applied inorganic fertilizers containing N, K\(_2\)O, and P\(_2\)O\(_5\) using standard methods for each region. The plants were harvested at maturity and divided into grains (unpolished rice) and straw for the metal analysis.

2.3. Pot experiments

The WT and \(lcd-kmt1\) seedlings were transplanted into 1/5000-a Wagner pots (one plant per pot) containing 3.0 kg of soil, which represented a 1:1 w/w mixture of soils that were naturally polluted with Cd and As, respectively. The Cd and As concentrations in the soil were 0.82 and 4.01 mg kg\(^{-1}\), respectively, after the mixture, determined using 0.1 M HCl extraction for soil Cd and 1 M HCl extraction for soil As. Each of six WT and \(lcd-kmt1\) plants were cultivated under flooded conditions until the heading stage, and then three of each group of plants were exposed to drained or continuously flooded conditions until harvest. The plants were divided into grains and straw for the Cd and As
analysis.

2.4. Evaluation of agronomic traits in the mutant rice

The plants were cultivated in a non-contaminated paddy field at the experimental field of the National Institute for Agro-Environmental Sciences under conventional intermittent irrigation until grain maturity. The planting density was 22.2 hills per m², with a spacing of 15×30 cm. A compound fertilizer containing 8% each of N, P₂O₅, and K₂O was applied as a basal dressing at rates of 50 kg ha⁻¹ N, P, and K. The chlorophyll contents in the flag leaf at the booting stage were determined using a SPAD meter (SPAD-502Plus, Konica Minolta Sensing, Inc., Tokyo, Japan). Agronomic traits were also measured: grain and straw yield, days to heading, plant height, culm length, and panicle number per plant. Sensory test of eating quality was conducted as follows: The cooked rice of lcd-kmt lines and WT was evaluated by a panel of 20 judges, who had been trained in the scoring of each component of eating quality. Because WT Koshihikari is the reference cultivar, all components (glossiness, smell, taste, stickiness, hardness, and overall evaluation) are scored 0. The scores from the 20 judges were averaged.

2.5. Analysis of Cd and other metals (As, Cu, Fe, Mn, and Zn)

The grain samples were air-dried and other samples (shoots and roots) were oven-dried at 70 °C. The mature shoot samples were milled to a fine power (to pass through a 0.5-mm mesh) using a stainless-steel rotor mill (P14, Fritsch Gmbh, Kastl, Germany). Sample digestion was performed as described previously (Ishikawa et al. 2005). Metal concentrations were determined by inductively coupled plasma-optical emission spectroscopy (Vista-Pro, Agilent Technologies Japan, Ltd., Tokyo, Japan) for Cu, Fe, Mn, and Zn or inductively coupled plasma mass spectroscopy (ELAN DRC-e, Perkin-Elmer Sciex, Concord, ON, Canada) for Cd and As. We used two certified standard materials to calibrate the concentrations of the metals in the rice samples: NIES CRM No. 10 rice flour (National Institute for Environmental Studies, Tsukuba, Japan) for Cd, Cu, Fe, Mn, and Zn and NIST CRM 1568a rice flour (National Institute of Standards and Technology, Gaithersburg, MD, USA) for As.

2.6. QTL mapping and sequencing

An F₂ population derived from a cross between a high-Cd indica cultivar (Kasalath) as the female parent and a low-Cd Koshihikari mutant (lcd-kmt1) as the male parent was used for QTL mapping. The F₂ progeny (92 seedlings) were treated with 0.18 µM CdSO₄ in a hydroponic system, as described above, and then small piece of the third leaf was collected for extraction of the genomic DNA. The remaining shoots and roots were harvested to analyze the metal concentrations.

Total RNA was extracted from the roots of the WT or lcd-kmt plants using Sepasol RNA I Super (Nacalai Tesque, Inc., Kyoto, Japan) following the manufacturer’s protocol. First-strand cDNA was synthesized from 1 µg of total RNA using ReverTra Ace (TOYOBO, Co., Ltd., Osaka, Japan) and oligo(dT)20 (TOYOBO) for the reverse-transcriptase polymerase chain reaction (RT-PCR). The full-length open reading frame (ORF) of OsNRAMP5 in the WT and lcd-kmt plants was amplified by means of PCR. The amplified full-length cDNAs were sequenced using an ABI 3130xl genetic analyzer (Applied Biosystems, Foster City, CA).

2.7. Development of genetic markers

Genomic DNA was extracted from fresh leaves of the WT, lcd-kmt1, and lcd-kmt2 plants. We designed primer pairs based on the sequences in the mutation regions for lcd-kmt1 or lcd-kmt2, respectively. The reaction mixture consisted of 20 to 50 ng of template DNA, 1× KAPA2GTM Fast ReadyMix with dye (Kapa Biosystems, Boston, MA, USA), and 300 nM of each amplification primer. PCR amplifications were performed as follows: initial denaturation for 2 min at 95 °C; followed by 30
cycles of 30 sec at 95 °C, 30 sec at 58 °C, and 10 sec at 72 °C; followed by a final extension for 20 sec at 72 °C. PCR products from the WT and *lcd-kmt1* plants were separated in sodium borate electrophoresis buffer in a 3% (w/v) agarose gel. The gel was stained with 1 mg/L ethidium bromide and visualized under UV light. The PCR products from the *lcd-kmt2* and WT plants were digested with the restriction enzyme FastDigest *Fsp*I (Thermo Scientific) in four times the volume of the digestion buffer, followed by electrophoresis in a 1% (w/v) agarose gel.

3. Results

3.1. Isolation of low-Cd accumulating rice mutants

We irradiated the most popular Japanese temperate *japonica* rice cultivar, Koshihikari, with accelerated carbon ions. Three low-Cd mutants (*lcd-kmt1*, *lcd-kmt2*, and *lcd-kmt3*) were identified in initial screening for grain Cd concentrations using 2592 M2 plants grown in Cd-polluted soil. The grain Cd concentration in wild-type (WT) Koshihikari averaged 1.73 mg kg⁻¹, versus values less than 0.05 mg kg⁻¹ in the three mutants. The three *lcd-kmt* mutants had identical phenotypes for metal concentrations. The root and shoot Cd and manganese (Mn) concentrations were significantly lower in *lcd-kmt* mutants than in the WT. Although the Mn concentrations were considerably lower than in the WT, there was no difference in plant growth except for *lcd-kmt3*. The concentrations of iron (Fe), zinc (Zn), and copper (Cu) of shoots and roots did not differ significantly between *lcd-kmt* mutants and the WT (Table 1). These results suggest that the *lcd-kmt* mutants exhibited decreased Cd uptake by their roots, and that Cd might be transported via the Mn pathway into the roots.

Table 1. Dry weights and metal concentrations in the shoots and roots of wild-type (WT) Koshihikari and of three low-Cd Koshihikari mutants (*lcd-kmt1*, *lcd-kmt2*, and *lcd-kmt3*) grown in hydroponic culture containing 0.18 μM Cd.

<table>
<thead>
<tr>
<th></th>
<th>Dry weight</th>
<th>Cd (mg kg⁻¹)</th>
<th>Mn (mg kg⁻¹)</th>
<th>Cu (mg kg⁻¹)</th>
<th>Fe (mg kg⁻¹)</th>
<th>Zn (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shoot</td>
<td>Koshihikari</td>
<td>0.071ab</td>
<td>45.8b</td>
<td>1004b</td>
<td>21.2a</td>
<td>57.5a</td>
</tr>
<tr>
<td></td>
<td><em>lcd-kmt1</em></td>
<td>0.081b</td>
<td>7.2a</td>
<td>79.3a</td>
<td>29.0b</td>
<td>58.5a</td>
</tr>
<tr>
<td></td>
<td><em>lcd-kmt2</em></td>
<td>0.087b</td>
<td>7.4</td>
<td>79.7a</td>
<td>28.2a</td>
<td>58.2a</td>
</tr>
<tr>
<td></td>
<td><em>lcd-kmt3</em></td>
<td>0.057a</td>
<td>6.5a</td>
<td>73.6a</td>
<td>27.7b</td>
<td>59.0a</td>
</tr>
<tr>
<td>Root</td>
<td>Koshihikari</td>
<td>0.024ab</td>
<td>205.4</td>
<td>113.0b</td>
<td>35.2a</td>
<td>297.6a</td>
</tr>
<tr>
<td></td>
<td><em>lcd-kmt1</em></td>
<td>0.026b</td>
<td>53.1a</td>
<td>29.9a</td>
<td>39.0a</td>
<td>281.3a</td>
</tr>
<tr>
<td></td>
<td><em>lcd-kmt2</em></td>
<td>0.027b</td>
<td>51.3a</td>
<td>30.2a</td>
<td>38.4a</td>
<td>255.5a</td>
</tr>
<tr>
<td></td>
<td><em>lcd-kmt3</em></td>
<td>0.019a</td>
<td>45.6a</td>
<td>30.0a</td>
<td>38.7a</td>
<td>291.4a</td>
</tr>
</tbody>
</table>

Data are the means of three replicates. Within a tissue type, numbers in the same column labeled with different letters differ significantly (*P* < 0.05, ANOVA followed by Tukey’s test).

3.2. Grain and straw metal concentrations of *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) (Fig. 1). The straw Cd concentrations were also much lower in *lcd-kmt1* and *lcd-kmt2* than in the WT (Fig. 2). Similar results were observed in the Cd concentrations in grains and straws *lcd-kmt3*. The grain Mn concentrations in *lcd-kmt* mutants was approximately one-third that of the WT, and an even greater difference (nearly 30 times) was observed.
in the straw Mn concentrations. The concentrations of Cu, Fe, and Zn in grains of \textit{lcd-kmt1} and \textit{lcd-kmt2} were similar to those of the WT. There was no significant difference in straw Fe concentration between the WT and \textit{lcd-kmt} mutants. Straw Zn concentrations seemed to be a little low in \textit{lcd-kmt1} and \textit{lcd-kmt2}.

In the pot experiment, flooded conditions significantly increased or decreased the concentrations of As or Cd, respectively, of grains and straws in both the WT and \textit{lcd-kmt1} (Table 2). Opposite patterns of As and Cd concentrations were observed in the WT grown under the drained conditions, whereas \textit{lcd-kmt1} showed simultaneously low levels of both Cd and As under such conditions.

Table 2: Grain and straw As and Cd concentrations of wild-type Koshihikari rice and the \textit{lcd-kmt1} mutant grown in soil contaminated with both metals under different water management conditions.

<table>
<thead>
<tr>
<th>Water management</th>
<th>Cultivars</th>
<th>As (mg kg(^{-1}))</th>
<th>Cd (mg kg(^{-1}))</th>
<th>As (mg kg(^{-1}))</th>
<th>Cd (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drained</td>
<td>Koshihikari</td>
<td>0.17</td>
<td>1.05</td>
<td>6.71</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>\textit{lcd-kmt1}</td>
<td>0.16</td>
<td>0.01</td>
<td>6.75</td>
<td>0.05</td>
</tr>
<tr>
<td>Flooded</td>
<td>Koshihikari</td>
<td>1.12</td>
<td>0.08</td>
<td>23.6</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>\textit{lcd-kmt1}</td>
<td>1.15</td>
<td>ND</td>
<td>24.4</td>
<td>ND</td>
</tr>
</tbody>
</table>

Drained conditions: The plants were cultivated under flooded conditions until heading, and under drained conditions from heading until harvest.

Flooded conditions: The plants were cultivated under continuously flooded conditions throughout the entire growth period.

ND, not detected (< 0.01 mg kg\(^{-1}\)).

3.3. Agronomic traits of \textit{lcd-kmt} mutants

The mutants were cultivated in the paddy field to evaluate whether agronomic traits such as grain yield and eating quality differed between the \textit{lcd-kmt} mutants and the WT plants. Among \textit{lcd-kmt mutants}, the characteristics of \textit{lcd-kmt3} apparently differed from that of the WT because of earlier
heading, smaller plant size, higher panicle numbers, and lower grain and straw yields than the WT. On the other hand, there were no apparent differences in plant morphologies and morphologies of rice grains of WT and *lcd-kmt1* or WT and *lcd-kmt2* (Fig. 2). In addition, no significant differences in SPAD value for chlorophyll content, plant height, culm length, and grain and straw yields were found between WT and *lcd-kmt1* or between WT and *lcd-kmt2* (Table 3).

![Fig. 2 Agronomic traits of Koshihikari and *lcd-kmt* mutants. (a) Plant morphologies of wild-type (WT) Koshihikari and *lcd-kmt1*. (b) Plant morphologies of wild-type (WT) Koshihikari and *lcd-kmt2*. (c) Morphologies of unhulled rice grains and unpolished rice grains.](image)

Table 3: Comparison of agronomic traits between Koshihikari and three low-Cd mutants (*lcd-kmt1*, *lcd-kmt2*, and *lcd-kmt3*).

<table>
<thead>
<tr>
<th></th>
<th>SPAD</th>
<th>Days to heading (days)</th>
<th>Plant height (cm)</th>
<th>Culm length (cm)</th>
<th>Panicle number/plant</th>
<th>Grain yield (t ha⁻¹)</th>
<th>Straw yield (t ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koshihikari</td>
<td>32.9ᵃ</td>
<td>85.4ᵇᶜ</td>
<td>103.4ᵇ</td>
<td>86.5ᵇ</td>
<td>13.2ᵃ</td>
<td>5.65ᵇ</td>
<td>7.74ᵇ</td>
</tr>
<tr>
<td><em>lcd-kmt1</em></td>
<td>33.2ᵃ</td>
<td>84.8ᵇ</td>
<td>105.3ᵇ</td>
<td>88.8ᵇ</td>
<td>13.4ᵃ</td>
<td>5.39ᵇ</td>
<td>7.38ᵇ</td>
</tr>
<tr>
<td><em>lcd-kmt2</em></td>
<td>32.9ᵃ</td>
<td>86.8ᵉ</td>
<td>104.0ᵇ</td>
<td>87.4ᵇ</td>
<td>13.7ᵃ</td>
<td>5.57ᵇ</td>
<td>7.43ᵇ</td>
</tr>
<tr>
<td><em>lcd-kmt3</em></td>
<td>30.6ᵇ</td>
<td>70.4ᵃ</td>
<td>91.7ᵃ</td>
<td>73.1ᵃ</td>
<td>16.3ᵇ</td>
<td>4.23ᵃ</td>
<td>4.78ᵃ</td>
</tr>
</tbody>
</table>

SPAD, chlorophyll content in the flag leaf determined using a SPAD meter. Values in the same column followed by different letters differ significantly (*P* < 0.05, ANOVA followed by Tukey’s test).

### 3.4. Gene identification

QTL analysis revealed that the QTLs related to low shoot and root Cd and Mn concentrations were co-localized on the short arm of chromosome 7. The peaks at the maximum logarithm of odds values for all traits were found at RM3767, which was located 9.07 Mbp from the distal end of the short arm of chromosome 7. We found two genes annotated as putative heavy-metal transporters (Os07g0257200 and Os07g0258400). The genes are *OsNRAMP5* (Os07g0257200) and *OsNRAMP1*
The **OsNRAMP1** cDNA sequence showed no alteration of this gene in the **lcd-kmt** mutants. On the other hand, the cDNA and genomic DNA sequences of **OsNRAMP5** revealed a single-nucleotide deletion in exon IX for **lcd-kmt2** and a 433-bp insertion in the terminal portion of exon X for **lcd-kmt1**. The latter replaced the terminal 32 bp in exon X with 50 bp in **lcd-kmt1**; the remaining 383 bp of the insertion was spliced out with intron X. An NCBI BLAST search showed that the insertion-DNA sequences agreed completely with **mPingA1** sequences that have been characterized as a new class of miniature inverted-repeat transposable element–like elements in rice (Kikuchi et al. 2003). The **OsNRAMP5** open reading frame of **lcd-kmt3** was not amplified by PCR and we found an approximately 227-kbp deletion that included all of **OsNRAMP5**. **OsNRAMP5** of the WT encoded a 538 amino acid (aa) protein. The single deletion in **osnramp5-2** results in aberrant translation of 53 aa before a new stop codon at aa 358. Interestingly, the **osnramp5-1** open reading frame was completely translated, but an 11-aa region of the wild-type was replaced with 17 aa (an increase of 6 aa) at the terminal position of exon X, resulting in a 544-aa region.

### 3.4. Development of genetic marker 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 between the WT and **lcd-kmt1** or between the WT and **lcd-kmt2** after FspI digestion, respectively. Since there is 433bp insertion in genomic region of **lcd-kmt1**, different PCR fragment patterns can be easily detected between **lcd-kmt1** and WT. The F1 heterozygous genotypes derived from **lcd-kmt1** x WT were detected by two bands on the gel. No different PCR fragments were observed between **lcd-kmt2** and WT. After FspI digestion, the PCR product of **lcd-kmt2** was cut at the specific restriction site for FspI, producing two fragments of the same size in the gel, whereas the PCR products of WT were not cut by this enzyme, thereby the F1 heterozygous genotypes derived from **lcd-kmt2** x WT can be detected.

### 4. Discussion

Using ion beams, new varieties of some flowers and trees have been previously commercialized, but in crops, there have not been put to practical use (Tanaka et al. 2010). By this technique, we first succeed to explore the non-transgenic rice mutants that accumulate nearly Cd-free in grains. Physiological studies in hydroponics indicated that the decreased root Cd uptake results in little amount of Cd in grains for mutants. Genetic analysis indicated that three mutants have different mutations of the same **OsNRAMP5**. This finding strongly suggests that mutation of **OsNRAMP5** greatly decrease Cd levels in rice grains. The **NRAMP** family of genes encodes integral membrane proteins in bacteria, fungi, plants, and animals (Cellier et al. 1995). Several NRAMP proteins functions as transporters of divalent metal ions, with broad substrate specificity (Thomine et al. 2000). In **Arabidopsis thaliana**, AtNRAMP1 is capable of transport of the multiple divalent metal ions such as Mn, Fe, and Cd. In our study, all **lcd-kmt** mutants exhibited the great reduced Mn levels in roots and shoots. Although there is a low similarity of deduced amino acid sequences between **OsNRAMP5** and AtNRAMP1, the common function for metal transport in the roots could be present. Interestingly, three different types of mutation, which are characterized by a transposon (**mPingA1**) insertion, point-like mutation, and large DNA deletion, were found on **OsNRAMP5**. The consensus transport motif in NRAMP protein has been suggested to be involved in the interaction with ATP-coupling subunits and to be important for metal transport by the NRAMP family of transporters (Curie et al. 2000). However, this motif was transformed into a hydrophobic segment in **osnramp5-1** and was incompletely present in **osnramp5-2**. In amino acid sequence in the motif, the Gly-347 residue on **OsNRAMP5** is absolutely conserved in all members of the NRAMP family and this residue could be especially important for the metal transport activity. However, this amino acid residue was not conserved in our rice mutants. Therefore, such changes might affect Cd and Mn transport via the cell membrane in the roots.

We were most concerned whether the **lcd-kmt** mutants grown in paddy fields exhibit excellent...
performance for grain Cd concentration with no significant differences in agronomic traits to the WT Koshihikari. Field trials showed that thelcd-kmtmutants have nearly undetectable Cd concentrations in their grains and straws. Surprisingly, there were no differences in the leaf chlorophyll content between WT andlcd-kmt1, although shoot Mn concentrations oflcd-kmtmutants drastically decreased as compared to those of WT. Rice is known to accumulate excess Mn without damage (Lidon et al. 2004), and the Mn concentration of rice shoots can be more than an order of magnitude higher than that of soybean shoots (Ishikawa et al. 2005). Presumably, rice may require less Mn for normal growth and can tolerate excess Mn induced by the reducing conditions in paddy soils.

The mutant plants oflcd-kmt1 andlcd-kmt2did not exert significant negative effects on plant or grain morphology, eating quality, grain yield, or straw yield. However,lcd-kmt3had earlier heading and smaller plant size than the WT, presumably because of the large DNA lesions in this accession. These results indicate thatlcd-kmt1 andlcd-kmt2can be used as practical rice plants. Therefore, we have appliedlcd-kmt2for rice variety registration in Japan and named it “Koshihikari Kan 1”. Moreover, we developed two DNA markers to detect polymorphism in the mutated genome region between the WT andlcd-kmt1and between the WT andlcd-kmt2. These can serve as a co-dominant marker, making it possible to detect both homozygous and heterozygous genotypes. Using thelcd-kmtmutants (lcd-kmt1 andlcd-kmt2) and the DNA markers, the breeding programs have been launched to confer the low-Cd trait into the popular Japanese cultivars (Akitakomachi, Hinohikari, Hitomebore, etc.) which are closely related to the Koshihikari.

If rice cultivars carrying the mutantnramp5alleles were cultivated throughout Japan, then dietary Cd derived from rice, which accounts for about half of the Japanese diet (Watanabe et al. 2004), would decrease greatly. Reeves and Chaney (2008) pointed out the high Cd availability of rice for humans because of relatively low Fe and Zn levels in rice-based diets. Nearly Cd-free rice in this study is not needed to consider the Cd availability in rice grains, rather another issue might occur on dietary Mn intake. A formal recommended dietary allowance (RDA) has not been set for Mn because of insufficient data. Therefore, an adequate intake (AI) of Mn has been estimated based on median intake. A formal recommended dietary allowance (RDA) has not been set for Mn because of insufficient data. Therefore, an adequate intake (AI) of Mn has been estimated based on median intake. A formal recommended dietary allowance (RDA) has not been set for Mn because of insufficient data. Therefore, an adequate intake (AI) of Mn has been estimated based on median intake. A formal recommended dietary allowance (RDA) has not been set for Mn because of insufficient data. Therefore, an adequate intake (AI) of Mn has been estimated based on median intake. A formal recommended dietary allowance (RDA) has not been set for Mn because of insufficient data. Therefore, an adequate intake (AI) of Mn has been estimated based on median intake. A formal recommended dietary allowance (RDA) has not been set for Mn because of insufficient data. Therefore, an adequate intake (AI) of Mn has been estimated based on median intake. A formal recommended dietary allowan ce (RDA) has not been set for Mn because of relatively low Fe and Zn levels in rice-based diets. Nearly Cd-free rice in this study is not decrease greatly. Reeves and Chaney (2008) pointed out the high Cd availability of rice for humans because of relatively low Fe and Zn levels in rice-based diets. Nearly Cd-free rice in this study is not needed to consider the Cd availability in rice grains, rather another issue might occur on dietary Mn intake. A formal recommended dietary allowance (RDA) has not been set for Mn because of insufficient data. Therefore, an adequate intake (AI) of Mn has been estimated based on median intake in males and females (Trumbo et al. 2001). The AI of Japan (4.0 and 3.5 mg day−1 for male and female, respectively) is about two-times high as that of USA and Canada (2.3 and 1.8 mg day−1 for male and female, respectively), indicating high Mn intake from diets for the Japanese. If the AI proposed by USA and Canada is sufficient to meet the Mn requirement, the decreased Mn level in the mutant rice might not greatly affect the adequate daily intake of Mn because, based on the current average rice consumption (160 g day−1) in Japan and the grain Mn concentration (approximately 9 mg kg−1) in thelcd-kmtplants, daily intake of Mn from the mutant rice would be approximately 60% of the adequate daily intake. In addition, dietary Mn is supplied from other gramineous crops, leguminous crops, vegetables, and seaweeds, so changes in its content in rice alone should not be a problem. Another advantage of using thelcd-kmtmutants is that As and Cd levels in rice will simultaneously decrease under early drainage conditions, and thereby potential risks of As and Cd for rice consumption people will reduce greatly. These mutant alleles can also be introduced intoindica cultivars, which are generally higher grain Cd concentrations than japonica cultivars, by means of marker-assisted selection. This technique would reduce the Cd concentrations in rice straw being fed to livestock, thereby greatly reducing bioaccumulation of Cd in meat. We therefore believe our findings represent an important tool for reducing the Cd level in paddy rice around the world (Ishikawa et al., 2012).

4. References


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Effect of iron plaque and rice genotypes on As accumulation in rice plants grown in As-contaminated paddy soils

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Abstract: The arsenic contamination of rice is received very much concern in recent years around the world. In this study, the effect of iron plaque formation on rice roots on the uptake and accumulation of As in rice seedlings and the comparison of iron plaque formation and As uptake capability of 28 rice genotypes grown in As-contaminated Guadu Plain paddy soils were investigated. In addition, As accumulation and speciation in rice grains of six rice genotypes were determined. The results show that iron plaque formation on rice roots can sequester most of As uptake from soils, reducing the accumulation of As in rice plants. It suggests that iron plaque is the main controlling factor in limiting the uptake of As into the rice plants grown in the As- contaminated Guandu Plain soils. There were significant differences in the amounts of Fe and As in iron plaque of rice roots among 28 tested rice genotypes, and 75.7-92.8 % of As uptake from soils could be sequestered in iron plaque. However, there was no significant negative correlation between the amounts of Fe in iron plaque and As in rice plants. It suggests that iron plaque formation capability of rice roots may be insufficient to predict the extent of As uptake and accumulation in rice plants among different rice genotypes. It was also found that As concentration in rice grains was influenced by As phytotoxicity, iron plaque formation capability of rice roots, and rice genotypes. In addition, arsenic species in rice grains were dimethylarsinic acid (DMA) and arsenite (As(III)), and the concentrations of DMA increased with total As concentrations, and conversely, the As(III) remained in the narrow range of 0.1 to 0.3 mg kg⁻¹.

Keyword: paddy rice, rice genotype, iron plaque, arsenic, arsenic species, Guandu Plain

1. Introduction

Inorganic arsenic (As) is identified as a non-threshold, class 1 human carcinogen, and the intake of As through consuming rice grain may lead to the serious health effects such as bladder and skin cancers (Mondal and Polya 2008; WHO 2004). The sources of As to paddy field including natural (biogeochemical process) and anthropogenic (As-containing irrigation water, metal mining activity, arsenical pesticide and fertilizer application) pathways (Bhattacharya et al. 2003). Rice is the dietary staple for about half of the world’s population and unfortunately, rice consumption has been the main arsenic exposure route in recent years (Mondal and Polya 2008; Williams et al. 2007a). This is due to the high bioavailability and mobility of As in flooding conditions, enhancing the uptake and accumulation of As by rice plants. (Xu et al. 2008). The concentration of As accumulated in rice grain approximately 10-fold larger than other cereal crops (Williams et al. 2007a, b). Meharg and Rahman (2003) found that the concentrations of As in rice grain grown in some part of Bangladesh As-contaminated soils was up to 1.8 mg kg⁻¹, thus it may resulted in the serious risk of As to residents. Moreover, paddy rice grown in As-contaminated also result in the As phytotoxicity (inhibition of ATP formation and oxidative stress) and grain yield reduction (Meharg and Hartley-Whitaker 2002; Panaullah et al. 2009).

Arsenic concentrations and species in paddy soil solutions are strongly dependent on the redox status (Meharg and Rahman 2003). In aerobic soils, arsenate (As(V)) is the predominant species and exists in low concentrations owing to its high affinity for soil minerals (Fitz and Wenzel 2002; Xu et al. 2008). However, in anaerobic conditions such as paddy soils, the predominant species is arsenite (As(III)). The mobility of As(III) in soils is increased due to the reductive dissolution of Fe oxides/hydroxides and As(V) reduction (Takahashi et al. 2004). In addition, soil properties such as pH, organic matter, clay content and poor crystalline iron oxides also affect the release of As into soil solutions (Bhattacharya et al., 2010; Bogdan and Schenk 2009; Takahashi et al. 2004; Sheppard 1992).

The formation of iron plaque on the roots of rice plants was observed and it was proposed that it may play an important role in limiting As uptake by paddy rice in the Guandu Plain (Wu, 2009). Iron plaque is commonly formed on the root’s surface of many aquatic plants, such as paddy rice (Hansel et al., 2001). Rice plants release oxygen into the rhizosphere via the aerenchyma which induces the precipitation of iron oxides/hydroxides on the root surfaces (Chen et al., 1980). Amorphous or crystalline iron (oxyhydr)oxides, such as 2-line ferrirhydrite and goethite, are the main components of
iron plaque (Hansel et al., 2001; Liu et al., 2006). Due to iron oxides/hydroxides strong affinity for arsenate, thus the iron plaque may sequester As and reduce its uptake into the root (Liu et al., 2004). The differences in the amounts of iron plaque formation on rice roots among different rice genotypes seem to be able to affect the extent of As uptake from soils. There were several studies that investigated the relationship between iron plaque formation on root and As uptake in rice plants for different genotypes of rice grown in hydroponic cultures (Lee et al. 2013; Wu et al. 2012). However, limited information is available on the effects of iron plaque formation on the uptake of As by different rice genotypes grown in As-contaminated soils.

In general, DMA and inorganic As are the predominant As species in rice grains (Zhao et al., 2010), and their percentages varied widely. Many studies investigated that the effect of rice genotypes and environment factor on the accumulation and speciation of As in rice grains (Ahmed et al. 2011; Norton et al. 2009a, b). Norton et al. (2009a) and Ahmed et al. (2011) reported that the environmental effect was the main controlling factor in grain As concentrations. Norton et al. (2009b) and Pillai et al. (2010) indicated that there were variation in grain As concentrations among different cultivars, and there were significant genotype effect on the As speciation in rice grains. In addition, the As phytotoxicity also impact on the accumulation and speciation of As in rice grains (Khan et al. 2010). In spite of that there were many studies reported about the As uptake and accumulation by rice, the soil As concentrations in most of these studies were below 100 mg kg⁻¹, and there were different results between the various field sites (Norton et al. 2009a). The mechanism of the difference in grain As accumulation, yield and As phytotoxicity among different rice genotypes grown in high As-contaminated soils is still unclear.

The objectives of this study were to investigate the effects of iron plaque formation on rice roots on the uptake and accumulation of As in rice seedlings grown in Guandu Plain soils, and to compare the differences in the amounts of iron plaque and capability of As uptake of 28 commonly rice genotypes planted in Taiwan and to investigate the effect on the As accumulation in rice seedlings. Finally, to investigate the influence of the genotypes and soil As concentrations on the As accumulation and speciation in rice grains.

2. Material and Methods

2.1 Soil sampling and characteristic
In this study, all As-contaminated soils were collected from surface soils (0-30 cm) of paddy rice fields in Guandu Plain, Taipei, Taiwan. The soils were classified based on USDA soil taxonomy as Umbric Albaqualfs, clay loam, mixed, thermic. The soils were air-dried, passed through 2 mm sieves, and stored in plastic vessels. Basic properties including soil pH (McLean 1982), texture (Gee and Bauder 1986), amorphous and crystalline Fe/Al oxides (Mckegue and Day 1966; Mehra and Jackson 1960), organic carbon (Nelson and Sommers 1982) and the total As concentrations in the soil (Meharg and Rahman 2003) were analyzed in this study. A certified reference material of soil (RTC CRM 025-250) was used to verify the recovery for soil As analysis.

2.2 Pot experiment
Twenty-eight rice (Oryza sativa L.) genotypes commonly planted in Taiwan, including fourteen japonica rice (TK 2, TK 4, TK 8, TK 9, TK 14, TK 16, TNG 16, TNG 67, TNG 71, TC 65, TC 192, TY 3, KS 139, and KS 145) and fourteen indica rice (TCN 1, TS 2, TCS 10, TCS 17, TCSW 1, TCSW 2, TCSY 112, TCSY 837, TCSY952031, TCSY 962021, TCSY 962024, TCSY 962037, TCSY 962045, and TCSY 962058), were used in this study.

Rice seeds were first sterilized in a solution containing 1% sodium hypochlorite and 1 drop of Tween 20 for 30 min, washed with deionized water and germinated in Petri dishes containing moist tissue paper for three days. After germination, rice seedlings were selected and transferred to a 0.6-L beaker and grown in half-strength modified Kimura B nutrient solution for 12 days. Five seedlings were then transplanted into per each pot filled with As-contaminated soils. Each pot contained 500 grams of tested soil. The soils were saturated with water and the water level was maintained at about 1-2 cm above the soil surface during the whole period of plant growth. The soils were supplemented with 260
mg N kg\(^{-1}\) as \((\text{NH}_4)_2\text{SO}_4\), 39 mg P\(_2\text{O}_5\) kg\(^{-1}\) as K\(_2\text{HPO}_4\) and 54 mg K\(_2\text{O}\) kg\(^{-1}\) as K\(_2\text{SO}_4\) as basal fertilizers. Rice seedlings were harvested at the 38th day after transplanting and were separated into roots and shoots. In addition, six rice genotypes including three japonica (TK 9, TC 192, TK 139) and three indica (TCN 1, TCSW 1, TCSY 837) genotypes grown in three As-level soils, and the mature rice was harvested nearly 130 days after transplantation. These samples were rinsed with tap water and then with deionized water. In order to avoid roots damage, we removed the roots from soils and rinsed it gently and rapidly. The fresh weights and lengths of each shoot and root were measured.

### 2.3 Soil solution collection and analysis

Soil pore water in the pots was collected by Rhizon soil moisture samplers (Rhizosphere Research Products) inserted into the soil near the middle of the container throughout the plant growth period. In order to prevent the precipitation of Fe ions and the change of As species, a portion of the solution was taken and preserved immediately in 5% HNO\(_3\) and 0.01 M H\(_3\)PO\(_4\) \cite{Daus2006}, respectively. The concentrations of Fe, As (As species) and dissolved organic carbon (DOC) were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 2000 DV, Perkin Elmer), high pressure liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS, LC 1200 and ICP-MS 7700x, Agilent Technologies) and total organic carbon analyzer (TOC analyzer, Aurora 1030W), respectively. The changes of soil pH and redox potential (Eh) were also monitored with flooding incubation. Five hundred grams of tested soils and 500 mL deionized water were put into plastic containers and incubated at room temperature (25 ± 2°C). A platinum electrode and a Ag/AgCl electrode (reference electrode) were used to measure the soil Eh during the flooding incubation period.

### 2.4 DCB (dithionite–citrate–bicarbonate) extraction of iron plaque

After harvesting the rice seedlings, the roots were washed with deionized water. One gram of fresh root was extracted in a DCB solution (40 mL 0.03 M sodium citrate and 0.125 M sodium bicarbonate, with an addition of 0.6 g sodium dithionite) for 1 hour at ambient temperature \cite{Liu2004}. The concentration of As and Fe in the DCB extracts were measured. In addition, one centimeter of fresh roots (middle part of roots) were cut and sliced for observation of the iron plaques’ localization and thickness using an optical transmission upright microscope.

### 2.5 Plant digestion and analysis

The root removed of iron plaque, shoot, flag leaf, grain (husk, bran, polished grain) were oven dried at 70°C for 48 hours, and ground to a fine powder. Dried plant samples (0.2- 1 g) were digested in concentrated HNO\(_3\)/H\(_2\)O\(_2\) in heating blocks \cite{Meharg2003}. The volume of the digests was brought up to 50-mL with deionized water and filtered through a 0.45 μm filter, and stored in plastic bottles for the subsequent analysis. The concentrations of Fe were determined by ICP-OES, and the concentrations of As was determined by ICP-MS. Certified reference materials of the plant sample (NSC DC73349) and rice flour (NIST 1568a) were used to verify the recovery of the digestion methods and elements analysis.

### 2.6 Determination of arsenic species in rice grains

Rice grain samples were extracted with 10 mL 0.28 M HNO\(_3\) placed in heating blocks at 95°C for 90 min \cite{Huang2010}. The reference material ERM BC-211 rice flour was used to check the extraction method. Arsenic species analysis standards used in this study including sodium meta-arsenite (NaAsO\(_3\), J.T. Baker), sodium arsenate dibasic heptahydrate (Na\(_2\)HAsO\(_4\)·7H\(_2\)O, Sigma), monosodium acid methane arsonate sesquihydrate (MMA, CH\(_4\)AsNaO\(_3\)·1.5 H\(_2\)O, Chem Service), and dimethylarsinic acid (DMA, C\(_2\)H\(_7\)AsO\(_2\), Chem Service). The matrix match standards and speciation extracts were determined by HPLC coupled to the ICP-MS. An anion-exchange column (PRP-X100, 250 × 4.1 mm, 10μm) from Hamilton Company (Reno, NV, USA) was used. The mobile phase was 20 mM NH\(_4\)H\(_2\)PO\(_4\), pH adjusted to 5.6 with NH\(_4\)OH. The injection volume was 50 μL, the flow rate was 1.5 mL min\(^{-1}\) and the temperature set at ambient temperature. In order to avoid the changes of As in the extracts, the samples was stored at 4°C in the dark, and all of the analyses were completed in 48 hours.
2.7 Data analyses
Data presented in this study are means (n = 3). Analysis of variance (ANOVA) was used to test the effect of soil As contents and rice genotypes on As accumulation in rice plants. For the comparison of the differences between treatments (soils or genotypes), we used the least significant difference (LSD) test at the level of P = 0.05. ANOVA and LSD tests were performed using the SAS 9.2 software package. Regression analyses were conducted using Excel for Windows.

3. Results and discussion

3.1 Iron plaque formation on the rice roots
Figure 1a shows the upright microscope images of the cross-section of the roots show that the reddish iron plaque is formed around the surface of rice roots grown in tested soils, mainly distributed in epidermis, exodermis and sclerenchyma cells of root (Syu et al., 2013). DCB extraction procedure has been widely used for the removal of iron plaque to determine the amount of iron plaque and As sorbed on iron plaque of roots (Liu et al. 2004; Wu et al. 2012). The image of a cross-section of roots after DCB extraction as shown in Figure 1b indicates that iron plaque could be removed effectively by using DCB solutions.

![Fig. 1. Upright microscope images of fresh rice root cross-sections showing (a) iron plaque on the root surfaces and (b) removal of iron plaque after DCB extraction](image)

3.2 Fe and As in iron plaque and rice plants of 28 rice genotypes
Figure 2a shows the amounts of iron plaque (expressed by DCB extractable Fe) accumulated on the root surfaces of the 28 rice genotypes grown in As-contaminated soil. The amounts ranged from 0.74 to 1.51 mmol Fe g\(^{-1}\) DW (dry weight). There were significant differences in the amounts of iron plaque among the tested genotypes of japonica (P<0.001) and indica (P<0.05) respectively. In addition, there were also significant differences in the amounts of As accumulated in the iron plaque among the tested genotypes of japonica (P<0.001) and indica (P<0.05) respectively (Syu et al., 2014). Table 1 indicates that that iron plaque formation on rice roots can sequester most of As uptake from soils, and 75.7-92.8 % of As uptake from soils could be sequestered in iron plaque. However, there was no significant negative correlation between the amounts of Fe in iron plaque and As in rice plants (Fig.3).
Fig. 2. The amounts of DCB extractable (a) Fe and (b) As of roots of 28 rice genotypes grown in Guandu Plain soils (156.6 mg As kg⁻¹). Data are means ± SD (n = 3). Different letters above the bars indicate significant difference in the value among the tested genotypes of japonica and indica respectively based on the LSD test (P < 0.05).
Table 1. The contents and distribution of As in different parts (iron plaque, roots, and shoots) of 28 rice genotypes grown in Guandu Plain soils (156.6 mg As kg⁻¹).

<table>
<thead>
<tr>
<th>Genotype</th>
<th>Iron plaque</th>
<th>Roots</th>
<th>Shoots</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Japonica</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KS 145</td>
<td>382.0 (89.1)*</td>
<td>34.9 (8.1)c</td>
<td>11.9 (2.8)c</td>
</tr>
<tr>
<td>KS 139</td>
<td>216.7 (88.6)a</td>
<td>16.4 (6.7)c</td>
<td>11.5 (4.7)b</td>
</tr>
<tr>
<td>TC 65</td>
<td>329.5 (75.9)c</td>
<td>89.8 (20.7)d</td>
<td>15.0 (3.4)bc</td>
</tr>
<tr>
<td>TC 192</td>
<td>460.3 (92.2)a</td>
<td>22.7 (4.6)c</td>
<td>16.0 (3.2)bc</td>
</tr>
<tr>
<td>TK 2</td>
<td>281.8 (89.2)c</td>
<td>22.5 (7.1)c</td>
<td>11.5 (3.7)bc</td>
</tr>
<tr>
<td>TK 4</td>
<td>372.3 (90.8)a</td>
<td>21.8 (5.3)c</td>
<td>15.7 (3.8)bc</td>
</tr>
<tr>
<td>TK 8</td>
<td>222.0 (88.3)a</td>
<td>17.6 (7.0)c</td>
<td>11.9 (4.7)b</td>
</tr>
<tr>
<td>TK 9</td>
<td>287.8 (89.4)a</td>
<td>22.1 (6.9)c</td>
<td>11.9 (3.7)bc</td>
</tr>
<tr>
<td>TK 14</td>
<td>328.7 (80.6)bc</td>
<td>64.9 (15.9)b</td>
<td>14.2 (3.5)bc</td>
</tr>
<tr>
<td>TK 16</td>
<td>268.3 (88.3)a</td>
<td>20.5 (6.7)c</td>
<td>15.1 (5.0)bc</td>
</tr>
<tr>
<td>TNG 16</td>
<td>337.1 (83.1)b</td>
<td>55.5 (13.7)b</td>
<td>13.2 (3.3)bc</td>
</tr>
<tr>
<td>TNG 67</td>
<td>370.4 (89.1)a</td>
<td>31.4 (7.6)c</td>
<td>13.7 (3.3)bc</td>
</tr>
<tr>
<td>TNG 71</td>
<td>155.5 (75.7)c</td>
<td>32.6 (15.9)b</td>
<td>17.4 (8.5)a</td>
</tr>
<tr>
<td>TY 3</td>
<td>398.2 (91.2)a</td>
<td>23.9 (5.5)c</td>
<td>14.6 (3.4)bc</td>
</tr>
<tr>
<td><strong>Indica</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TC 2</td>
<td>256.0 (84.4)c</td>
<td>40.7 (13.4)b</td>
<td>6.7 (2.2)cd</td>
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<tr>
<td>TCN 1</td>
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<td>19.6 (4.8)g</td>
<td>9.8 (2.4)cd</td>
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<tr>
<td>TCS 10</td>
<td>310.6 (92.1)bce</td>
<td>17.7 (5.2)g</td>
<td>8.9 (2.6)bced</td>
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<tr>
<td>TCS 17</td>
<td>378.6 (93.2)a</td>
<td>21.2 (5.2)g</td>
<td>6.7 (1.6)d</td>
</tr>
<tr>
<td>TCSW 1</td>
<td>381.4 (92.7)ab</td>
<td>22.9 (5.6)g</td>
<td>7.3 (1.8)d</td>
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<tr>
<td>TCSW 2</td>
<td>263.4 (91.0)bce</td>
<td>19.4 (6.7)g</td>
<td>6.6 (2.3)bcd</td>
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<tr>
<td>TCSY 112</td>
<td>303.5 (88.8)ed</td>
<td>30.8 (9.0)ed</td>
<td>7.4 (2.2)ed</td>
</tr>
<tr>
<td>TCSY 837</td>
<td>199.8 (87.2)de</td>
<td>22.9 (10.0)f</td>
<td>6.4 (2.8)bced</td>
</tr>
<tr>
<td>TCSY 962021</td>
<td>423.8 (91.7)bce</td>
<td>30.0 (6.5)g</td>
<td>8.6 (1.9)cd</td>
</tr>
<tr>
<td>TCSY 962024</td>
<td>168.5 (76.6)f</td>
<td>42.3 (19.2)a</td>
<td>9.3 (4.2)a</td>
</tr>
<tr>
<td>TCSY 962031</td>
<td>275.0 (88.3)de</td>
<td>27.4 (8.8)ed</td>
<td>9.1 (2.9)bc</td>
</tr>
<tr>
<td>TCSY 962037</td>
<td>401.5 (89.2)ed</td>
<td>39.9 (8.9)cde</td>
<td>8.8 (2.0)ed</td>
</tr>
<tr>
<td>TCSY 962045</td>
<td>228.4 (89.7)bced</td>
<td>18.9 (7.4)def</td>
<td>7.4 (2.9)bced</td>
</tr>
<tr>
<td>TCSY 962058</td>
<td>150.7 (85.2)f</td>
<td>18.8 (10.6)f</td>
<td>7.3 (4.1)ab</td>
</tr>
</tbody>
</table>

Content (μg As plant⁻¹): As concentration (μg As/ g) × biomass (g/plant)

Distribution (%): [As contents / (As contents in iron plaque + As contents in roots + As contents in shoots)] x 100

*Different letters indicated the differences among the rice genotypes of japonica and indica were significant based on the LSD test (P < 0.05).

TF: As contents in shoots / As contents in roots
The results of this study indicate that there were differences in the As retention in iron plaque and As uptake by rice plants among the 28 tested rice genotypes grown in Guandu Plain soils. Although the iron plaque on rice roots can sequester most of As uptake from soil no matter what genotypes of rice used in this study, the iron plaque formation capability of rice roots may be insufficient to predict the extent of As uptake and accumulation in rice plants among different rice genotypes. The genotypes with low As uptake capability selected from this study could be recommended for planting in As-contaminated soils (Syu et al., 2014).

3.3 Influence of soil As levels and rice genotypes on the As concentrations of rice grains

The As concentrations in grains (polished) in As-L soils was higher than As-M and As-H soils and there were significant differences among the three tested soils. The grain As concentrations of the six tested genotypes grown in As-M and As-H soils was reduced 40.4 % and 35.0 % respectively compared with As-L soils (Fig. 4). The lower As concentrations in the grains of the six tested rice
genotypes grown in As-M and As-H soils compared to As-L soils may result from the As phytotoxicity of rice plants grown in high As concentration soils (As-M and As-H soils), as shown in Figure 5. Khan et al (2010) and Panaullah et al (2009) also found that the phytotoxicity of As in rice plants resulted in the reduction of As accumulation in the rice grains. This result indicates a higher As uptake and translocation efficiency in rice grains grown under normal (low As toxicity) growth conditions compared to those in high As toxicity soils. This observation is similar to those found in the study of Khan et al (2010) who reported that high concentrations of As accumulated in rice grains grown in low As concentration Bangladeshi soils (<20 mg kg⁻¹). In our pot experiment, the soils were flooding throughout the entire growth period. This can also enhance As release from soils, and further lead to the accumulation of As in rice grains (Arao et al., 2009).

Fig. 4. The concentrations of As in grain (polished grain) of six tested rice genotypes grown in the three levels of As contaminated soils of Guandu Plain. Data means ± standard deviation (n = 3). Different small and capital letters above the bars indicate significant difference in the values among the tested soils and rice genotypes respectively based on the LSD test (P < 0.05). (As-L: 16.3 mg As kg⁻¹, As-M: 343.3 mg As kg⁻¹, As-H: 512.3 mg As kg⁻¹.)
Fig. 5. The (a) root length, (b) shoot height and (c) grain yield of six tested rice genotypes grown in the three levels of As contaminated soils of Guandu Plain. Data means ± standard deviation (n = 3). Different small and capital letters above the bars indicate significant difference in the values among the tested soils and rice genotypes respectively based on the LSD test (P < 0.05). (As-L: 16.3 mg As kg⁻¹, As-M: 343.3 mg As kg⁻¹, As-H: 512.3 mg As kg⁻¹.)

The grain As concentrations of indica genotypes (0.88 ± 0.04 mg kg⁻¹) were higher than japonica genotypes (0.71 ± 0.02 mg kg⁻¹) grown in As-L soils. TCSW1 (0.92 ± 0.04 mg kg⁻¹) and KS 145 (0.68 ± 0.01 mg kg⁻¹) had the highest and lowest concentrations of As in rice grains, respectively (Fig. 4). The results indicate that the As uptake and translocation capability of the indica genotypes are higher than japonica genotypes grown in low As-contaminated soils. However, there is no significant difference in grain As concentrations between indica genotypes and japonica genotypes grown in
As-M and As-H soils. This possibly results from As uptake and translocation capabilities in rice plants being affected by As phytotoxicity.

### 3.4 As species distribution in rice grains of different genotypes

Since As species distribution in rice grains govern the toxicity to humans, thus it is important to know the distribution of As species in rice plants. Figure 6 shows As species distributed in polished grains, it indicates that the predominant As species in the polished grains were DMA (45.6-80.2 %) and As(III) (19.8-54.4 %). It was also discovered that the concentrations of DMA in grains increased with total As concentrations of grains of the six tested rice genotypes grown in the three As level soils ($R^2=0.9091$, $P<0.001$), but the concentrations of As(III) remained in the narrow range of 0.1 to 0.3 mg kg$^{-1}$ (Fig. 7). These findings indicate that the translocation and accumulation of As(III) into grains may be restricted while the total grain As concentrations increase. The results are similar to the study of Khan et al (2010), but differing from Meharg et al. (2009) who found that the inorganic As in rice grains increases with total As concentrations of grains. The different results of the various studies may result from environmental factors and rice genotypes (Ahmed et al., 2009; Norton et al., 2009a). Carey et al (2010) also indicate that the translocation of DMA from shoot to grain is much more efficient than inorganic As.

The results of this study indicate that due to phytotoxicity, low level of As was accumulated in polished grain grown in elevated As-contaminated Guandu Plain soils. In addition, the concentrations of As in rice grains of indica genotypes are higher than japonica genotypes, suggesting that japonica genotypes are recommended for planting in As-elevated paddy soils. The predominant As species found in rice grains are DMA and As(III), and the percentage of DMA increases with total As concentrations in rice grains. Because the toxicity of DMA is lower than that of inorganic As species, the health risk may not be increased through consumption of rice even as the total As content in grains is increased.

![Fig. 6. The percentage of As species in grain (polished grain) of six tested rice genotypes grown in the three levels of As contaminated soils of Guandu Plain. (As-L: 16.3 mg As kg$^{-1}$, As-M: 343.3 mg As kg$^{-1}$, As-H: 512.3 mg As kg$^{-1}$.)](image)
Fig. 7. Regression between the concentrations of total As and As species in grains (polished grain) of six tested rice genotypes grown in the three levels of As contaminated soils of Guandu Plain.

Acknowledgements
The financial support from the National Science Council, Executive Yuan, Taiwan (grant no. NSC-101-2313-B-002-012-MY3) is sincerely appreciated.

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Comparison of various single chemical extraction methods for predicting the bioavailability of arsenic in paddy soils

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Abstract: The Codex Committee of Contaminants in Food (CCCF) has been discussing a new standard for arsenic (As) in rice since 2010 and a code of practice for the prevention and reduction of As contamination in rice since 2013. Therefore, our current studies focus on setting a maximum level of As in rice and paddy soil by considering bioavailability in the remediation of As contaminated soils. We study mitigation techniques including optimal water management during rice cultivation, soil amendment management, selection of low As rice varieties, and measuring As in rice during processing and cooking. This study aimed to select an appropriate single chemical extractant for evaluating the mobility of As in paddy soil and the bioavailability of As to rice. Nine different extractants, such as deionised water, 0.01 M Ca(NO3)2, 0.1 M HCl, 0.2 M C6H8O7, 0.43 M HNO3, 0.43 M CH3COOH, 0.5 M KH2PO4, 1 M HCl, and 1 M NH4NO3 were used in this study. Total As content in soil was also determined after aqua regia digestion. The results of As extraction ability was in the order of: Aqua regia > 1 M HCl > 0.5 M KH2PO4 > 0.43 M HNO3 > 0.2 M C6H8O7 > 0.1 M HCl > 0.43 M CH3COOH > deionized water > 1 M NH4NO3 > 0.01 M Ca(NO3)2. Correlation between soil extractants and As content in rice was in the order of: deionized water > 0.01 M Ca(NO3)2 > 0.43 M CH3COOH > 0.1 M HCl > 0.5 M KH2PO4 > 1 M NH4NO3 > 0.2 M C6H8O7 > 0.43 M HNO3 > 1M HCl > Aqua regia. BCF (bioconcentration factor) according to extractants was in the order of: 0.01M Ca(NO3)2 > 1 M NH4NO3 > deionized water > 0.43 M CH3COOH > 0.1 M HCl > 0.43 M HNO3 > 0.2 M C6H8O7 > 0.5 M KH2PO4 > 1 M HCl > Aqua regia. Thus, 0.01 M Ca(NO3)2(r=0.78**) by single extraction was shown to have the potential for predicting As bioavailability in soil with higher correlation between As in rice and the extractant.

Key words: Arsenic, Paddy soil, Bioavailability, Single extraction method

1. Introduction

The Ministry of Environment established the criteria of soil contamination for heavy metal(loid)s in the agricultural fields designated by the Soil Environment Conservation Law in 1996 (MOE, 1996). The Ministry of Food and Drug Safety also established the criteria of 0.2 mg/kg for cadmium (Cd) in polished rice in Korea (KFDA, 2000). Recently, our regulations for agricultural environment including soil, irrigation water, agricultural materials (fertilizer and compost etc.), and agricultural products are being gradually reinforced (KFDA, 2011; MOE, 2010a). The CCCF (Codex Committee of Contaminants in Foods) have been under discussion on the maximum levels for arsenic (As) in polished rice since 2010 (FAO/WHO, 2014).

In Korea, the standard method of analyzing heavy metal(loid)s contamination in soils is by aqua regia digestion (MOE, 2010b). This method is acceptable to evaluate the environmental burden of pollutants to the soil and to decide the proper environmental management and human safety. However, this method is not useful for assessing the metal bioavailability to crops. In order to minimize the risk of heavy metal(loid)s to the agricultural environment, crops, livestock, and humans exposed during the agricultural activities, considering bioavailability for the remediation of heavy metal(loid)s is necessary for agro-food safety (Naidu et al., 2003; Heemsbergen et al., 2009; Kim et al., 2009; Salazar et al., 2012; Bolan et al., 2014). Even though the development of analytical methods for measuring the bioavailability of heavy metal(loid)s in agricultural soils was rare in Korea, various assessment techniques were already developed worldwide. Bioavailability of metal(loid)s in agricultural soils was determined mainly by the concentration of metal(loid)s, the species and fractions of a specific metal(loid), and the physico-chemical properties of soils (Ruby et al., 1993; Geebelen et al., 2002; Kim et al., 2012a). Various single and stepwise sequential extraction methods were suggested to estimate the bioavailability of heavy metal(loid)s in agricultural soils. The Soil Environment Conservation Law recommended the use of 0.1 M HCl for Cd, lead (Pb), copper (Cu), chromium (Cr), nickel (Ni), and zinc (Zn) and 1.0 M HCl for As to evaluate their bioavailability (MOE, 2002). It was reported by regression analysis that the bioavailability of Cd and Zn to rice was higher than those of
Cu and Pb. It was also concluded that the 0.1 M HCl extractable heavy metal(loid)s in soil were more closely correlated with heavy metal(loid)s in husked rice than 0.1 M HNO₃, 0.005 M DTPA and 0.05 M EDTA extractable heavy metal(loid)s in soil (Jung et al., 2000). It was also reported that the 0.01 M Ca(NO₃)₂ extraction method was effective than the 1 M NH₄NO₃ extraction method for the bioavailability of Cd and other metal(loid)s in soils (Seo et al., 2013). However, there are few studies on the As bioavailability in agricultural soils in Korea. Therefore, the objectives of this study were (i) to propose a suitable single extraction method for assessing the bioavailability of As in soils, (ii) to verify the physico-chemical factors affecting As uptake and its transformation to rice, and (iii) to finally identify and develop the countermeasure techniques to conserve the As contaminated paddy soils.

2. Materials and Methods

2.1. Soil and rice sampling

The three As contaminated sites (MB, SS, TC) were selected based on the result of a detailed survey at the 300 abandoned mines by the Ministry of Environment during 2007 - 2009 due to high concentration of As (MOE, 2007 ~ 2009). Soil and rice samples were collected within a 100 - 1,000 m distance from each site in 2012. All soil samples comprised of 3 – 6 sub-samples collected within a depth of 15 cm from the surface in each mine site. Soil samples were air-dried, crushed, passed through a 20-mesh sieve, and ground with a mortar. The harvested rice samples were air-dried, polished with a rice mill (Husked : SYTH88, Ssangyong Instrument, Korea, Polished : McGill miller, HT McGill Inc, USA), and then pulverized with a homogenizer.

2.2. Soil properties

The soil pH value was measured at the ratio of 1:5 soil:deionized water suspension using pH meter (250A, Thermo Orion, Beverly, MA). The soil organic matter (SOM) was determined by Tyurin method with K₂Cr₂O₇ (Tyurin, 1931). The exchangeable cations, i.e. calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), were measured using 1 N ammonium acetate at pH 7.0, and analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, GBC XMP, Australia) (NIAST, 2000).

2.3. Determination of arsenic in soil and rice

Standard reference material (SRM; Contaminated soil BAM-U112; BAM Federal Institute for Materials Research and Testing, Berlin, Germany) and 3 g soil samples were acid digested with aqua regia as described by the Ministry of Environment (MOE, 2010b). Aqueous soil samples were filtered with Whatman No. 5B filter, and analyzed for As using hydride generation (HG) -ICP-OES (GBC XMP, Australia). To compare the bioavailability of As in paddy soils, nine different soil extractants such as deionized water, 0.01 M Ca(NO₃)₂, 0.1 M HCl, 0.2 M C₆H₈O₇, 0.43 M HNO₃, 0.43 M CH₃COOH, 0.5 M KH₂PO₄, 1 M HCl, and 1 M NH₄NO₃ were used (Table 1). Soil extracts were continuously shaken at 30°C for 1 h, filtered with Whatman No. 5B filter, and analyzed by HG-ICP-OES. The accuracy of As in SRM was 8.41 ± 0.52 with certified values of 10.4 ± 0.4 mg/kg. The recovery values of As was 81.27 ± 4.98. 0.5 g of polished rice samples were transferred into a high pressured-polytetrafluoroethylene (PTFE) vessel and digested with 8 mL of 70% HNO₃ and 1 mL H₂O₂ (Sigma-Aldrich, St. Louise, MO) using microwave digestion system (ETHOS, Milestone, Italy). After cooling to room temperature, the extracts were filtered through a 0.45-μm membrane filter, and adjusted to a final volume of 25 mL. The As contents in polished rice were determined by ICP-MS (Agilent technologies 7500a). The SRM accuracy value of As was 0.29 ± 0.05 with certified value of 0.29 ± 0.03 mg/kg. Extraction efficiencies (%), determined by dividing the extracted As content by total As content were 100.58 ± 17.59.
Table 1. Single extracting solutions of arsenic in soil.

<table>
<thead>
<tr>
<th>Extraction solution</th>
<th>SSR²</th>
<th>Time (hour)</th>
<th>Temp. (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>1:50</td>
<td>16</td>
<td>20</td>
<td>Mackovych et al. (2003)</td>
</tr>
<tr>
<td>0.01M Ca(NO₃)₂</td>
<td>1:2</td>
<td>2</td>
<td>20</td>
<td>Seo et al. (2013)</td>
</tr>
<tr>
<td>0.1M HCl</td>
<td>1:5</td>
<td>1</td>
<td>30</td>
<td>MOE (2002)</td>
</tr>
<tr>
<td>0.2M C₆H₈O₇</td>
<td>1:5</td>
<td>0.5</td>
<td>20</td>
<td>Amofah et al. (2010)</td>
</tr>
<tr>
<td>0.43M HNO₃</td>
<td>1:10</td>
<td>1</td>
<td>20</td>
<td>Tippinga et al. (2003)</td>
</tr>
<tr>
<td>0.43M CH₃COOH</td>
<td>1:40</td>
<td>16</td>
<td>20</td>
<td>Quevauviller et al. (1997)</td>
</tr>
<tr>
<td>0.5M KH₂PO₄</td>
<td>1:20</td>
<td>0.5</td>
<td>20</td>
<td>Giri et al. (2012)</td>
</tr>
<tr>
<td>1M HCl</td>
<td>1:5</td>
<td>0.5</td>
<td>30</td>
<td>MOE (2002)</td>
</tr>
<tr>
<td>1M NH₄NO₃</td>
<td>1:2.5</td>
<td>2</td>
<td>20</td>
<td>DIN (1995), Itanna et al. (2008)</td>
</tr>
</tbody>
</table>

²: Soil to solution ratio

2.4. Calculation of bioconcentration factor (BCF)

Bioconcentration factor (BCF, Eq. 1) is defined as the ratio of the As concentration in crops (mg/kg DW) and soil (mg/kg DW) considering the crop uptake from soils and its transformation to the edible part of crops (Kim et al., 2012b).

\[
\text{Bioconcentration factor (BCF)} = \frac{\text{As conc.in rice (mg/kg)}}{\text{As conc.in soil (mg/kg)}} \quad \text{(Eq. 1)}
\]

2.5. Calculation of soil-water partition coefficient for arsenic (Kd)

The soil water partition coefficient (Kd, Eq. 2) describes the partitioning of As over two phases (Naidu et al., 1994; Sauve et al., 2000; Krishnamurti and Naidu, 2000). Equation 3 was used in this study to estimate the As bioavailability in soil.

\[
\text{Partitioning coefficient (K_d)} = \frac{\text{Solid phase concentration of metals}}{\text{Solution phase concentration of metals}} \quad \text{(Eq. 2)}
\]

\[
\text{Partitioning coefficients (K_d)} = \frac{\text{Total conc.of As in soil (mg/kg)}}{\text{Bioavailable As content in soil (mg/kg)}} \quad \text{(Eq. 3)}
\]

2.6. Statistical Analysis

Single and multiple regression analysis were performed using SPSS statistical program ver. 12.0 (SPSS Co., Chicago, IL) to investigate the influence of soil characteristics, i.e. pH, organic matter, and exchangeable cationic As contents in soil and rice. In regression analysis, the total and extractable As contents in soil, and As concentration in rice were log₁₀-transformed to make homogeneous variances.

3. Results and Discussion

3.1. Soil Characteristics

The results of characterized soil samples (n=30) are as follows: soil pH ranged from 5.1 to 7.5, SOM contents ranged from 3.79 to 37.85 g/kg dry soil, with a mean value of 22.51 g/kg dry soil. This value was slightly lower than 26.0 g/kg which was the average content of paddy soils in Korea. The concentration of cations ranged between 0.12 - 10.02 cmol+/kg for Ca, 0.21 - 2.05 cmol+/kg for K, 0.20 - 5.27 cmol+/kg for Mg, and 0.21 - 1.65 cmol+/kg for Na (Table 2). Soil pH 7.0 of paddy soils near SS mine was higher than 5.5 of MB mine and 5.6 of TC mine. Ca and Mg content in SS paddy soil were also higher than those of MB and TC mine. It means there was soil reclamation activity for
the metalloid(s) contaminated paddy soils near SS mine by the addition of lime material.

Table 2. Chemical properties of the soils used in this study.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>OM</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave.</td>
<td>5.78</td>
<td>22.51</td>
<td>4.58</td>
<td>0.62</td>
<td>1.46</td>
<td>0.38</td>
</tr>
<tr>
<td>Min.</td>
<td>5.09</td>
<td>3.79</td>
<td>0.12</td>
<td>0.21</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>Max.</td>
<td>7.48</td>
<td>37.85</td>
<td>10.02</td>
<td>2.05</td>
<td>5.27</td>
<td>1.65</td>
</tr>
<tr>
<td>Average for paddy soil⁷</td>
<td>5.9</td>
<td>26</td>
<td>5.1</td>
<td>0.30</td>
<td>1.30</td>
<td>0.35</td>
</tr>
<tr>
<td>Optimal range⁷</td>
<td>5.5-6.5</td>
<td>25-30</td>
<td>5.0-6.0</td>
<td>0.25-0.30</td>
<td>1.5-2.0</td>
<td></td>
</tr>
</tbody>
</table>

⁷: RDA, 2011.

3.2. Arsenic Contents in Soils and Polished Rice

Average content and range of As in the surveyed paddy soils were 26.87 and 10.90 - 88.92 mg/kg, respectively. It was found out that thirteen samples among 30 exceeded the As concern level for soil contamination described in the Soil Environment Conservation Act. Average content and range of As in the surveyed rice were 0.09 and 0.03 - 0.23 mg/kg, respectively (Table 3). This value was quite similar with the results surveyed near abandoned mine area in 2000 with an average As content of 0.10 mg/kg and was slightly higher with the results surveyed in the non-contaminated area in 2001 with an average As content of 0.06 mg/kg (Kim et al., 2007). These values were also below the 0.2 mg/kg maximum permitted concentration for inorganic As by Codex Committee of Contaminants on Food (CCCF) considering 76.94% (54.50 - 87.86%) of the ratio of inorganic As against total As in polished rice in Korea (FAO/WHO, 2014: Kim et al., 2013).

Table 3. Total arsenic content in soil and polished rice.

<table>
<thead>
<tr>
<th></th>
<th>Total As content in soil</th>
<th>Total As content in rice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave.</td>
<td>26.87</td>
<td>0.09</td>
</tr>
<tr>
<td>Min.</td>
<td>10.90</td>
<td>0.03</td>
</tr>
<tr>
<td>Max.</td>
<td>88.92</td>
<td>0.23</td>
</tr>
<tr>
<td>Average for paddy soil⁶</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Concern level in area ¹⁰</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

⁶: RDA, 2011.  

3.3. Arsenic Contents in Soils using Single Extraction Method

To compare bioavailability of As in paddy soils, 9 different soil extractants were employed. Extractants of As that have widely been used are deionized water, 0.01 M Ca(NO₃)₂, 0.1 M HCl, 0.2 M C₆H₈O₇, 0.43 M HNO₃, 0.43 M CH₃COOH, 0.5 M KH₂PO₄, 1 M HCl, 1 M NH₄NO₃ as mentioned in Table 1. Average content and range of As extracted with 9 extractants are shown in Table 4.

Table 4. Arsenic contents according to single extracting solution.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Deionized water</th>
<th>0.01M Ca(NO₃)₂</th>
<th>0.1M HCl</th>
<th>0.2M C₆H₈O₇</th>
<th>0.43M HNO₃</th>
<th>0.43M CH₃COOH</th>
<th>0.5M KH₂PO₄</th>
<th>1M HCl</th>
<th>1M NH₄NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave.</td>
<td>0.181</td>
<td>0.013</td>
<td>0.665</td>
<td>2.132</td>
<td>2.455</td>
<td>0.497</td>
<td>3.357</td>
<td>5.489</td>
<td>0.018</td>
</tr>
<tr>
<td>%¹</td>
<td>67</td>
<td>0.05</td>
<td>2.47</td>
<td>7.93</td>
<td>9.14</td>
<td>1.85</td>
<td>12.49</td>
<td>20.43</td>
<td>0.07</td>
</tr>
<tr>
<td>Min.</td>
<td>0.010</td>
<td>0.001</td>
<td>0.040</td>
<td>0.220</td>
<td>0.170</td>
<td>0.020</td>
<td>0.410</td>
<td>0.330</td>
<td>0.001</td>
</tr>
<tr>
<td>Max.</td>
<td>1.440</td>
<td>0.112</td>
<td>6.830</td>
<td>11.824</td>
<td>14.25</td>
<td>6.140</td>
<td>14.75</td>
<td>30.04</td>
<td>0.197</td>
</tr>
</tbody>
</table>

¹: Average As content (%) of each extractant against total As in soil

The As concentration of soils by using single extraction procedures was in the order of 1 M HCl > 0.5 M KH₂PO₄ > 0.43 M HNO₃ > 0.2 M C₆H₈O₇ > 0.1 M HCl > 0.43 M CH₃COOH > deionized water.
> 1 M NH₄NO₃ > 0.01 M Ca(NO₃)₂. 1 M HCl was able to extract As ranging between 3 and 34% where higher extractability was observed for highly contaminated soil. Elliott and Shastri (1999) reported that the overall extent of metal solubilization increased modestly as the system became more acidic. Other researchers suggested low molecular weight organic acid and phosphate salts were more effective in extracting As, attaining more than 40% extraction in the pH range of 6 – 8 (Bhattacharya et al., 2002; Alam et al., 2001; Stroud et al., 2011). Bioconcentration factors (BCF) of soil to rice according to various single extracting solutions are shown in Table 5. Crop transformation of As were more affected by the extractable As content than total As in soils which predicts the bioavailability of As in soils (Savie et al., 1996: Brun et al., 1998: McLaughlin et al., 2000). Currently, the BCF calculations established by USEPA, UKEA, RIVM were used for the purpose of environmental risk assessment in Korea (USEPA, 1992: USEPA, 1996: CLEA, 1998: Otte et al., 2001). USEPA reported that the empirical BCF for As in only one sample of grains and cereal, specially sorghum, was 0.026 in the sludge treated soil. This value was absolutely different with 0.004 of rice BCF in this study. It was probably attributed to the varietal and species difference. Kim et al. (2012b) reported that the average transfer coefficient of As to the rice was 0.309 against 0.1 M HCl extractable As in soil. This value was similar with 0.405 value in this study. The BCF value calculated with various extractants by using single extraction procedures was in the order of 0.01 M Ca(NO₃)₂ > 1 M NH₄NO₃ > deionized water > 0.43 M CH₃COOH > 0.1 M HCl > 0.43 M HNO₃ > 0.2 M CaH₂O₇ > 0.5 M KH₂PO₄ > 1 M HCl. It appeared that 0.01 M Ca(NO₃)₂ extraction was a better option for the determination of bioavailable metal(loid)s in soils. Lee et al. (2012) reported various patterns of crop uptake and transformation of heavy metal(loid)s with different crop species, varieties, parts, growing seasons, plowing, and irrigation methods. Table 6 showed the regression equations between BCF of As according to extracting solutions and soil chemical properties in order to identify the factors affecting BCF in the presence of different extractants. Deionized water extraction was affected by SOM (r=0.52**) while 0.01 M Ca(NO₃)₂ was affected by both SOM (r=0.65***) and exchangeable Na (r=0.71***) 1 M HCl extraction was also affected by SOM (r=0.61***) and exchangeable Na (r=0.68***) with higher coefficients. Most of the extractants were affected by exchangeable Na including 0.1 M HCl (r=0.60***) and 0.2 M CaH₂O₇ (r=0.58**), 0.43 M HNO₃ (r=0.56**), 0.43 M CH₃COOH (r=0.53**), 0.5 M KH₂PO₄ (r=0.47**) and 1 M NH₄NO₃ (r=0.62**). In summary, while exchangeable Na was the major factor which affected the BCF of various extractants, the impact of SOM towards the BCF was also significant. Zeng et al. (2012) reported that several factors, such as soil texture, physiological characteristics of crops, physico-chemical properties of soil, heavy metal(loid) content and binding form, decisively affected the BCF. Gonzaga et al. (2012) observed that while SOM and Mg concentrations were positively correlated to plant As accumulation, Ca concentration was negatively correlated.

Table 5. Bioconcentration factor (BCF) of soil to rice according to extracting solution.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Deionized water</th>
<th>0.01M Ca(NO₃)₂</th>
<th>0.1M HCl</th>
<th>0.2M CaH₂O₇</th>
<th>0.43M HNO₃</th>
<th>0.43M CH₃COOH</th>
<th>0.5M KH₂PO₄</th>
<th>1M HCl</th>
<th>1M NH₄NO₃</th>
<th>Total As in soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave.</td>
<td>1.036</td>
<td>16.713</td>
<td>0.405</td>
<td>0.094</td>
<td>0.095</td>
<td>0.523</td>
<td>0.041</td>
<td>0.039</td>
<td>13.664</td>
<td>0.004</td>
</tr>
<tr>
<td>Min.</td>
<td>0.110</td>
<td>2.075</td>
<td>0.034</td>
<td>0.008</td>
<td>0.006</td>
<td>0.038</td>
<td>0.005</td>
<td>0.003</td>
<td>1.185</td>
<td>0.001</td>
</tr>
<tr>
<td>Max.</td>
<td>5.668</td>
<td>94.467</td>
<td>1.540</td>
<td>0.243</td>
<td>0.333</td>
<td>2.834</td>
<td>0.141</td>
<td>0.172</td>
<td>70.850</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Table 6. Regression equation between bioconcentration factor (BCF) of arsenic according to extracting solution and soil chemical properties.

<table>
<thead>
<tr>
<th>Regression equation</th>
<th>R</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>0.52**</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>0.01M Ca(NO₃)₂</td>
<td>0.65***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>Log(BCF-DW) = 0.091-0.770Log(OM⁴)</td>
<td>0.52**</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>Log(BCF-0.01M Ca(NO₃)₂) = 1.346-1.043Log(OM)</td>
<td>0.65***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>Log(BCF-0.01M Ca(NO₃)₂) = 1.561-0.690Log(OM)+0.649Log(Na)</td>
<td>0.71***</td>
<td>&lt;0.000</td>
</tr>
</tbody>
</table>
0.1M HCl
Log(BCF-0.1M HCl) = -0.010+1.187Log(Na)

0.2M C₆H₈O₇
Log(BCF-0.2M C₆H₈O₇) = -0.660+1.069Log(Na)

0.43M HNO₃
Log(BCF-0.43M HNO₃) = -0.667+1.109Log(Na)

0.43M CH₃COOH
Log(BCF-0.43M CH₃COOH) = 0.017+0.995Log(Na)

0.5M KH₂PO₄
Log(BCF-0.5M KH₂PO₄) = -1.167+0.663Log(Na)

1M HCl
Log(BCF-1M HCl) = -1.028+1.184Log(Na)

Table 7 shows the partition coefficients (Kd) of arsenic according to single extraction method. The partition coefficients of extractants by using single extraction procedures were in the order of 0.01 M Ca(NO₃)₂ > 1 M NH₄NO₃ > deionized water > 0.43 M CH₃COOH > 0.1 M HCl > 0.43 M HNO₃ > 0.2 M C₆H₈O₇ > 0.5 M KH₂PO₄ > 1 M HCl. When the partition coefficients are low, the amount of heavy metal(loid)s absorbed on to the soil particle is also low compared with the amount of heavy metal(loid)s in soil solution. Table 8 showed the regression equation between Kd of As according to extracting solution and soil chemical properties in order to identify the factors affecting partition coefficients with different extractants. Deionized water extraction was negatively correlated with exchangeable K (r=0.53 ***) and positively correlated with exchangeable Mg (r=0.64 **). 0.01 M Ca(NO₃)₂ extraction was negatively correlated with exchangeable K (r=0.76 *** ) and SOM (r=0.72 *** ) and positively correlated with exchangeable Na (r=0.80 *** ). 1 M HCl extraction was negatively correlated with SOM (r=0.72 *** ) and positively correlated with exchangeable Na (r=0.78 *** ). Therefore, exchangeable K, exchangeable Na and SOMr were the major factors affecting the partition coefficients of various extractants similar to the observation made for BCF. Yang et al. (2012) noticed that Kd values varied widely in As-contaminated paddy soils and correlated well with soil pH, SOM and total As. In another study, Fu et al. (2011) reported that grain As concentrations correlated significantly to soil As speciation, SOM and soil P contents.

3.4. Calculation of partition coefficients with various extractants

Table 9 shows the regression equations between As contents in rice, and extracting solutions and soil chemical properties to find the factors affecting As concentration in rice. The As content extracted by single extraction procedures was correlated in the order of deionized water > 0.01 M Ca(NO₃)₂ > 0.43 M CH₃COOH > 0.1 M HCl > 0.43 M HNO₃ > 0.2 M C₆H₈O₇ > 0.5 M KH₂PO₄ > 1 M HCl > Aqua regia. It means that the uptake and transformation of As to rice was more effective with bioavailable form of As than total As in soil. Among the single extractants, deionized water and 0.01 M Ca(NO₃)₂ highly correlated with As concentration in rice and therefore, be a possible extractant to measure the bioavailability of As in soils. By comparing the total amount of rice and extracting solution content, and the relationship between the soil chemical properties, deionized water, 0.01 M Ca(NO₃)₂, 0.1 M HCl, 0.2 M C₆H₈O₇, 0.43 M CH₃COOH, 0.5 M KH₂PO₄, and 1 M NH₄NO₃ solutions are independent of the substitution and was found to be affected by the exchangeable cation, respectively. Shin (2003) also reported that exchangeable ion, which was the absorbed form on soil particle and easily exchangeable with other ions, desorbed or changed to ion form in soil solution by pH or the change of surface charge on soil particle.

Table 7. Partition coefficients (Kd) of arsenic according to extracting solution.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Deionized water</th>
<th>0.01M Ca(NO₃)₂</th>
<th>0.1M HCl</th>
<th>0.2M C₆H₈O₇</th>
<th>0.43M HNO₃</th>
<th>0.43M CH₃COOH</th>
<th>0.5M KH₂PO₄</th>
<th>1M HCl</th>
<th>1M NH₄NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave.</td>
<td>279.52</td>
<td>4317.29</td>
<td>112.28</td>
<td>24.91</td>
<td>25.18</td>
<td>148.15</td>
<td>10.39</td>
<td>9.84</td>
<td>3546.75</td>
</tr>
<tr>
<td>Min.</td>
<td>42.06</td>
<td>538.86</td>
<td>8.87</td>
<td>4.96</td>
<td>4.25</td>
<td>9.86</td>
<td>4.21</td>
<td>2.62</td>
<td>307.76</td>
</tr>
<tr>
<td>Max.</td>
<td>1324.33</td>
<td>22072.22</td>
<td>412.56</td>
<td>60.52</td>
<td>77.90</td>
<td>662.17</td>
<td>26.58</td>
<td>40.13</td>
<td>16554.2</td>
</tr>
</tbody>
</table>
Table 8. Regression equation between partition coefficients (K_d) of arsenic according to extracting solution and soil chemical properties.

<table>
<thead>
<tr>
<th>Regression equation</th>
<th>R</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deionized water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-DW) = 2.103 - 0.985 Log (K)</td>
<td>0.53**</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Log (K_d-DW) = 2.049 - 1.051 Log (K) + 0.427 Log (Mg)</td>
<td>0.64**</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td><strong>0.01M Ca(NO_3)_2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-0.01M Ca(NO_3)_2) = 3.783 - 0.927 Log (OM³)</td>
<td>0.72***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>Log (K_d-0.01M Ca(NO_3)_2) = 3.612 - 0.783 Log (OM) - 0.542 Log (K)</td>
<td>0.76***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>Log (K_d-0.01M Ca(NO_3)_2) = 3.753 - 0.554 Log (OM) - 0.540 Log (K) + 0.422 Log (Na)</td>
<td>0.80***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td><strong>0.1M HCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-0.1M HCl) = 2.352 + 0.966 Log (Na)</td>
<td>0.53**</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td><strong>0.2M C_6H_8O_7</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-0.2M C_6H_8O_7) = 1.701 + 0.848 Log (Na)</td>
<td>0.57**</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Log (K_d-0.2M C_6H_8O_7) = 1.469 + 0.723 Log (Na) - 0.726 Log (K)</td>
<td>0.67***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td><strong>0.43M HNO_3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-0.43M HNO_3) = 1.501 - 0.828 Log (OM)</td>
<td>0.54**</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td><strong>0.43M CH_3COOH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-0.43M CH_3COOH) = 2.379 + 0.774 Log (Na)</td>
<td>0.45*</td>
<td>&lt;0.012</td>
</tr>
<tr>
<td>Log (K_d-0.43M CH_3COOH) = 2.108 + 0.629 Log (Na) - 0.846 Log (K)</td>
<td>0.57**</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td><strong>0.5M KH_2PO_4</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-0.5M KH_2PO_4) = 1.111 - 0.455 Log (OM³)</td>
<td>0.61***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td><strong>1M HCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-1M HCl) = 1.143 - 0.962 Log (OM)</td>
<td>0.72***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>Log (K_d-1M HCl) = 1.321 - 0.669 Log (OM) + 0.538 Log (Na)</td>
<td>0.78***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td><strong>1M NH_4NO_3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-1M NH_4NO_3) = 3.873 + 0.936 Log (Na)</td>
<td>0.62***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>Log (K_d-1M NH_4NO_3) = 3.662 + 0.822 Log (Na) - 0.661 Log (K)</td>
<td>0.69***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>Log (K_d-1M NH_4NO_3) = 3.096 + 0.641 Log (Na) - 0.869 Log (K) + 0.666 Log (Ca)</td>
<td>0.75***</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td><strong>Total As in soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (K_d-Total) = 1.280 + 0.353 Log (OM)</td>
<td>0.44*</td>
<td>&lt;0.013</td>
</tr>
</tbody>
</table>

Table 9. Regression equation between arsenic contents in rice, and extractants and soil chemical properties.

<table>
<thead>
<tr>
<th>Regression equation</th>
<th>R</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deionized water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.859 + 0.163 Log (DW-As) + 0.309 Log (K)</td>
<td>0.49*</td>
<td>&lt;0.023</td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.759 + 0.197 Log (DW-As) + 0.307 Log (K) + 0.139 Log (Na)</td>
<td>0.51*</td>
<td>&lt;0.046</td>
</tr>
<tr>
<td><strong>0.01M Ca(NO_3)_2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.323 + 0.295 Log (0.01M Ca(NO_3)_2-As) + 0.278 Log (Na)</td>
<td>0.49*</td>
<td>&lt;0.031</td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.411 + 0.227 Log (0.01M Ca(NO_3)_2-As) + 0.251 Log (Na) + 0.296 Log (K)</td>
<td>0.53*</td>
<td>&lt;0.021</td>
</tr>
<tr>
<td><strong>0.1M HCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.944 + 0.115 Log (0.1M HCl-As) + 0.366 Log (K)</td>
<td>0.48*</td>
<td>&lt;0.040</td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.810 + Log (0.1M HCl-As) + 0.345 Log (K) + 0.220 Log (Na)</td>
<td>0.51*</td>
<td>&lt;0.029</td>
</tr>
<tr>
<td><strong>0.2M C_6H_8O_7</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.998 + 0.088 Log (0.2M C_6H_8O_7-As) + 0.416 Log (K)</td>
<td>0.44*</td>
<td>&lt;0.048</td>
</tr>
<tr>
<td><strong>0.43M CH_3COOH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.928 + 0.122 Log (0.43M CH_3COOH-As) + 0.358 Log (K)</td>
<td>0.47*</td>
<td>&lt;0.030</td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.815 + 0.169 Log (0.43M CH_3COOH-As) + 0.348 Log (K) + 0.177 Log (Na)</td>
<td>0.50*</td>
<td>&lt;0.049</td>
</tr>
<tr>
<td><strong>0.5M KH_2PO_4</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (Total As in rice) = -1.058 + 0.164 Log (0.5M KH_2PO_4-As) + 0.408 Log (K)</td>
<td>0.48*</td>
<td>&lt;0.026</td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.993 + 0.218 Log (0.5M KH_2PO_4-As) + 0.422 Log (K) + 0.169 Log (Na)</td>
<td>0.51*</td>
<td>&lt;0.046</td>
</tr>
<tr>
<td><strong>1M NH_4NO_3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (Total As in rice) = -0.787 + 0.102 Log (1M NH_4NO_3-As) + 0.401 Log (K)</td>
<td>0.46*</td>
<td>&lt;0.040</td>
</tr>
</tbody>
</table>
Therefore, exchangeable ion would be a major factor affecting the uptake of heavy metal(loid)s to crop. In conclusion, single extraction using 0.01 M Ca(NO₃)₂ was shown to be effective for predicting As bioavailability in soil with higher correlation between As in rice and the extractant.

4. Conclusion

Until now, the standard method of analyzing heavy metal(loid)s contamination in soils is by aqua regia digestion. This method is acceptable to evaluate the environmental burden of pollutants to the soil and to decide the proper environmental management and human safety. However, this method is not useful for assessing the metal bioavailability to crops. This study aimed to select an appropriate single chemical extractant for evaluating the mobility of As in paddy soil and the bioavailability of As to rice and to finally establish a new criteria of heavy metal(loid) contamination in soil considering the bioavailability to crops. It was concluded that 0.01 M Ca(NO₃)₂ single extraction was effective in predicting As bioavailability in soil with higher correlation between As in rice and the extractant.

5. Acknowledgement

This study was financially supported by “Research Program for Agricultural Science & Technology Development (Project No. PJ 009219)” National Academy of Agricultural Science, Rural Development Administration, Korea.

6. References


New Regulation Development for Soil Remediation of Heavy Metal Contaminated Sites and Health Risk-based Approaches in Taiwan

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Abstract: In this article, we introduced the basis of establishing soil pollution control standard (SPCS or regulation) of heavy metals and described the present regulatory control standard of heavy metals in rural soils and general soils in Taiwan. An integrated assessment of the soil pollution control standards of heavy metals was made and the new revisions have been suggested. The new revisions will be more concerned about risk-based approach regulation, crop production, food security and food safety, the status of soil background and also the soil properties of the contaminants which may be hazardous in different pathways for different land uses. The concentrations of Cu and Zn in the edible parts of the crops are not harmful to human health before the crop productivity have significantly reduced, which was produced by the phytotoxicity and consequently, the SPCS of soil Cu and Zn can be kept at presented values or be revised to optimize the economic benefits of management soil resources with the prerequisite of food safety. Cr(VI) and Cr(III) can produce health risks with a large difference of toxicity and harmfulness and should be concerned individually for the risk control of high potential Cr-contaminated soils. Addition of the SPCS of As, Cd, Cr(VI), Cu, Hg, Ni, and Pb in industry park area was also recommended according to the lower risks which accept higher metal levels in this area compared with present SPCS for normal lands and rural lands. The potential contaminated area of Taiwan can decrease without posing higher health risks. The SPCSs of As and Pb in the rural soils and also in the normal area or industrial park were suggested to be lower values based on the risk-based approach results in different land uses. In the normal land, it is suggested to decrease the SPCS level of Hg, to add the new SPCS of soil Cr(III) and Cr(VI) based on the risk assessment of the site. The new revising approach of SPCS are concerning the health risks, crop toxicity, economic benefit and environmental effects can reduce the total area of potential contamination. It may also provide an efficient soil survey and management strategies for soil resources.

Keywords: heavy metals pollution, soil pollution control standard (SPCS), regulation, new revision, health risk assessment

1. Introduction

Industrial pollution sites have been found in Taiwan since 1981 and Taiwan has encountered continuous events of soil and groundwater pollution caused by arbitrary disposal of wastewater and wastes mainly discharged from industrial parks. The serious events on the headlines included the industrial pollution resulted from Taiwan Petrochemical Development Corporation (TPDC), Go-In Chemical Industrial Co., Ltd., Chee-Li Chemical Corp., RCA, and other illegal waste disposal sites throughout the Taiwan in 1980s. Therefore, the issues on the soil and groundwater environment protections were highly concerned by the governmental officers, research scientists, and also resident near the pollution sites in Taiwan. After many years of discussions and revisions, the Legislative Yuan of Taiwan approved the Soil and Groundwater Pollution Remediation Act in 1999 and officially announced the new Act into law in January, 2000. According to this Act, soil quality standards were announced in January, 2001.

The Legislature established a system where soil and groundwater pollution sites will be divided into two categories. In Taiwan’s regulation, two soil levels of each concerned heavy metal were set for pollution management, which were the lower level of Soil Pollution Monitoring Standard and the higher level of Soil Pollution Control Standard. When levels of soil or groundwater pollution exceed Soil Pollution Control Standards, the site will be listed as a "control site", and the competent authority will be responsible for taking measures to prevent the pollution from further extension. After the control site was assessed as to high risk site, then it will be listed as a "remedial site", and the pollution producer will be asked to remediate the site based on this Act. Moreover, the related land transfer of the pollution site also was prohibited. Up to the end of 2013, more than 4,430 farmland pollution sites were announced as control sites and 2,021 sites of them were cancelled from the announced control sites list (Taiwan EPA, 2014). For the soils with pollution levels higher than the Soil Pollution Monitoring Standards but still lower than the Soil Pollution Control Standards, monitoring projects...
should be continuously conducted. Because of the urgency for legislating regulations and environment protection in Taiwan, the control standards were set referring to the soil regulations over the world and also several local researches in Taiwan. In addition, the zoning management was also included.

In the last decade, the implement of the Soil and Groundwater Pollution Remediation Act was successfully used to control and manage the pollution sites which reached the short-term objective to reduce the risk of the sites. However, for a long-term management of pollution control, the Soil Pollution Control Standards needs to be revised while an integrated concern factors should be involved or communicated with different agencies and communities, which include social and economic transition, land productivity, human health risk assessment, soil characteristics, contaminant properties, and the crucial efficiency of executive and remedial processes. In this paper, some criteria and bases for regulation establishment of heavy metals in soils were introduced. We also described the regulation and present soil standards in Taiwan. The health risk-based approaches were conducted and finally, the suggested revisions of the control standards of metals of soils were discussed.

2. Factors for regulation establishment of heavy metals in soils

In order to revise the regulations and limit levels of heavy metals in soils, there are several factors to be concerned. An excess of heavy metals in agro-ecosystems might result in agricultural products with unacceptable quality levels which might be harmful to food chain, and even reduced crop yields (Alloway, 1990; Fergusson, 1990; Chen, 2012a, 2012b). High level concentrations of heavy metals in soil might affect the soil organisms activities, including microorganisms (Bååth, 1989), nematodes (Bengtsson and Tranvik, 1989) and earthworms (Ma and van der Vooet, 1993). It may also cause increasing effects on metals in surface water, drinking water or aquatic organisms, respectively (Crommentuijn et al., 1997).

The direct concern of the effects of soil heavy metals pollution may be the land use efficiency, especially for crop productivity and food safety. Because heavy metal pollutions may cause decrease of crop yields and farmers' income, it is common to develop the limit levels based on phyto-toxicity of heavy metals. However, in a soil ecosystem, soil organisms could be sensitive to the heavy metals despite it might be not easily observed. The presence of heavy metals in soils can be harmful to the soil biota and then decrease the soil biodiversity. Therefore, the assessments of the ecological toxicity from heavy metals have been developed and the assessing system can be used to establish relative regulations and limit levels. In certain conditions, the heavy metal levels were not resulting from toxicity to crop or drops in yields while un-ignorable accumulation in the edible tissues had been occurred which resulted in the dangerous food chain. The pollution levels might also include serious human health risks via other exposure pathways. Consequently, the limit levels of heavy metals in soils can be set according to the results of health risk assessments. For a rural land, risks caused from the high levels of heavy metals in edible parts of crops would be more critical than other types of land use. However, the uncertainty of the relationship between heavy metal level in soils and uptake by crops can also lead to the difficulties of setting the limit levels.

Carlon (2007) indicated a worldwide review of derivation methods of soil screening values which showed that the risk assessment was the most frequently concerned. In the other hand, the economic and executive resources are precious and often limited, and thus too strict regulations or captious limit levels probably result the waste of these resources, the decreases in the efficiency of soil pollution management, and may restrict the social/economic development. Therefore, to formulate the relative regulations and limit levels of heavy metals, an integrated concern as described above should be conducted to consider the scientific, technologic, economic, and social factors. Moreover, the regulations and limit levels should be able to be revised to accommodate environment and social changes and to provide the maximum efficiency of total resources with the premise of safety of human beings.

2.1 Metal effects on crop productivity (phyto-toxicity)

Biosolids are regarded to the treated matters of green wastes or sewage sludge and often contain high levels of organic matter and several nutrients. In the USA, the land disposal of biosolids has been used and popularized in last few decades. However, it also contain different heavy metals and thus the regulation of biosolids usage and relative limit levels has been developed based on the results of a large number of researches. McBride (2003) illustrated the concepts of relationships between heavy
metals and plants and also denoted the uncertainty of predicting the plant uptake using soil levels of heavy metals. Ideally, the heavy metal concentration of plant tissue is related to the crop growth or yields. Drop of yield was occurred when crop was accumulated certain heavy metal to a toxic level. **Fig. 1** shows the conceptual diagram of the described relationship (McBride, 2003). In the USA, the acute toxicity threshold (50% growth reduction in a short term plant bioassay) was proposed which is quite unacceptable for the farmers. For maintaining the farmer benefits (economic concern), a more tolerable endpoint of less than 10% yield loss may be acceptable. However, because of the growth variation caused by other environmental, cultivation and crop variety factors are generally high, a statistical significant reduction of crop growth or yield might be higher than 20%. Furthermore, the crop species may reveal quite different response or sensitivity to the metal toxicity. The differences in the metal toxic levels regarded to economic, statistical, and real yield reductions are much smaller for the abrupt type than the gradual type of crops. Therefore, the establishment of metal toxic levels for abrupt type crops is easier and less controversial than the gradual type.

A conceptual diagram of the maturing effects was given in **Fig. 2**, which indicated that heavy metal toxicity might be different to the crops in various growth stages (Davis-Carter et al., 1991). Briefly, growth of seedlings and older plants may be more sensitive to the heavy metal uptake than the young plants. In addition, the various response of different part of a plant to heavy metals can be observed. For some crop species, the root growth is related to metal uptake while the growth of shoots or yields of grain is not. The adverse response for root and top of a crop may also exist. The conceptual diagram was given in **Fig. 3** (Dragun and Baker, 1982). Although the toxic effect of a heavy metal to crops may be complicated, a toxic level could be identified according to an unacceptable yield loss which is coordinated by farmers, agricultural scientists, economists, and environmental pollution managers. As shown in **Fig. 4**, an uncertainty was calculated which means the probability that unacceptable loss of yields still occur when the heavy metal concentration in tissues is lower than the identified toxic levels. The higher toxic level was set, the higher probability of false assurance should be obtained. To insure the availability of a toxic level of certain heavy metal in crop tissue, 5% of the false assurance probability may be used.
There is a relationship between the heavy metal concentrations in soils and in plant tissues as shown in Fig. 5, and hence the toxic levels in soils or the soil limit levels of heavy metals should be regarded to the toxic level in plant tissues which was described above. However, the establishment of toxic levels of heavy metals in soils will be more difficult because of the complexity of soil-plant barriers theory. Soil properties are known to directly affect the heavy metal uptake by crops (Nan et al., 2002; Chen, 2012a, 2012b) and also indirectly affect on the plant growth caused by different soil nutrient availability. For example, dissoluble organic carbon (DOC) can affect the heavy metal mobility in crops (Lee and Chen, 2010) and consequent availability in soils. Again, the different response of plant part, genetic nature, and maturation to heavy metals in soils may exist. Furthermore, the heavy metal concentration of tissues will significantly decrease the crop productivity, which with higher heavy metal supply from the toxicity into the roots and consequently inhibit the translocation from roots to shoots (Fig. 5). The plant species may also show different uptake response to the metal contents of soil. Conceptual diagram of three categories of these metal uptake responses were shown in Fig. 6. A plant categorized as the sensitive type can uptake a certain heavy metal quickly and reaches the toxic level of tissues in soils with low concentration of the metal element. In contrast, a plant which can survive and not accumulate high level of heavy metal in soil environments with high metal content is categorized as a tolerant type. A plant which has linear relationship between heavy metal content in tissue and in soils can be regarded as a good indicator plant of soil pollutants (Chen and Guo, 2011).

![Fig. 5. A conceptual relationship between heavy metals in tissues and in soils.](image1)

![Fig. 6. Conceptual diagram of different plant response to heavy metal content in soils.](image2)

The uncertainty of toxic levels of heavy metals in tissue and in soils also includes soil aging effects. Briefly, two hypotheses were developed in the published references (Fig. 7). The uptake plateau concept (Chang et al., 1984, 1997) is based on the low availability of heavy metals in soils and that application of biosolid also provides more adsorption capacity into soils. Therefore, heavy metal uptake by plant reaches a plateau and soil system provides a hidden margin of safety. Several long-term studies with similar results were found (Brown et al., 1998; Dowdy et al., 1994). Pichtel and Anderson (1997) also showed that Cu and Zn uptake by crops is less than 4% of the amount added with sludge applications. On the other hand, McBride (1995, 2003) denoted that the uncertainty of soil environment is important while the adsorption condition of heavy metals may change over time. For example, when soil organic matter is decomposed or the soil is acidic, certain heavy metals might be released into the soil and then the absorbed metals by plant which may produce high risk for the food safety. The concept is like a time-bomb. The description of this section shows the approaches and difficulty of establishing the toxic levels of heavy metals in plant tissues and also in the soils. A simplified approach was shown in Fig. 8, which can be used to set up the limit value to protect the crops against unacceptable reducing yield which was caused by the metal toxicity. The scattered diagram between yield and metal concentration in soils can be made and after the unacceptable yield loss and soil limitation are set, the probability of false assurance can be calculated which indicate that unexpected low yields may be occurred even though the heavy metal level is still lower than the limit. Accordingly, the soil limit of heavy metals in soils can be adjusted to obtain an acceptable probability of false assurance. The lower probability is accepted, the more critical limit value is obtained. Commonly, the 5% of the probability of false assurance may be used to maintain land productivity.
2.2 Ecological toxicity (species sensitivity distributions, SSD)

Soil organisms are usually sensitive to soil heavy metals despite the phenomena might be not easily observed. Assessment approaches were established for identify the background level or reference values of heavy metals in soils (De Vries et al., 2004; Groenenberg et al., 2006; Mol et al., 2012). The presence of heavy metals can be harmful to the soil biota and then decrease the soil biodiversity. Therefore, the assessment of the ecological toxicity from heavy metals in soils was developed and the assessing system can be used to establish the relative regulations and limit levels. First, the response of crop species to a soil pollutant should be quantified and the common method would be regarded as the dose-response assessment. Several critical values of dose response can be used to indicate the toxicity of a soil pollutant. For example, lethal dose (LD50) and (LC 50) indicate the acute toxicity by the amount and concentration of a soil pollutant required to produce the 50% reduction of the studied pollutant. In addition, the no-observed effect concentration (NOEC) indicates the chronic toxicity and is determined of the highest concentration of a test pollutant which has no statically significant effect on the soil organisms comparing to a control site. For a given pollutant concentration, the potentially affected fraction (PAF) of the species having lower NOECs to all the tested species can be calculated. The species sensitivity distribution (SSD) curve of the environment can be established with various concentrations of the pollutant (Fig. 9). An environmental concern about the ecological toxicity is often used by setting the PAF at 5%. According to the SSD curve, the 5% PAF regarded concentration of a certain pollutant can be obtained which is served as a hazardous concentration (HC5).

Fig. 7. Conceptual diagram of the aging effect of soils on heavy metal uptake by plant (drawn based on the description of McBride, 2003)

Fig. 8. A simplified method to obtain soil limit value of heavy metals to deal with the uncertainty of the relationship between heavy metal level in soils and yields.

Fig. 9. An example of the diagram of species sensitivity distribution from the no observed effect concentration (NOEC) data. PAF: potentially affected fraction. EQC: environmental quality concern. HC5: hazardous concentration which can result in 5% of PAF. (Mol et al., 2012)
This value can be used as a reference value, background value or target value for pollution management. The regulatory control standard or soil limit value of a pollutant can be set at numbers of folds of the reference value or using a higher PAF to obtain the seriously hazardous concentration (e.g. HC$_{30}$). Recatalá et al. (2010) discussed the feasibility of soil quality standards of heavy metals established based on the reference values and showed that it might result in much higher levels in crops than the food safety levels or acceptable phyto-toxicity levels in certain cases.

In Netherland, an assessment system was well developed to formulate the reference values of heavy metals in soils. The PAFs were tested and found to be well correlated to the active metal concentration in soils (0.43 M HNO$_3$ extractable) but not to the total concentration of heavy metals. To evaluate the active concentration, the metal concentration in topsoil was assumed to include two fractions. One is native which presents with original soil minerals while the other is enrichment which is adventitious. As examples shown in Fig. 10, good relationships were found between the total concentration of each heavy metal and Al$_2$O$_3$ in subsoil. The consistent linear relationship between metal to Al$_2$O$_3$ in subsoil was assumed to be resulted from their native-origin and was used to estimate the native fractions of metals in topsoil by using the Al$_2$O$_3$ concentration in topsoil and the correlation line in subsoil. The enrichment of heavy metals in topsoil was then obtained from the total metal content divided by its native fraction. The heavy metal enrichment was then found to well correlate to their active concentrations (i.e. the adventitious fraction may be more available or mobile). Accordingly, the active concentration of heavy metals in the topsoil can be estimated. The SSD curve among the PAF and active concentration of each heavy metal was then established as shown in Fig. 11 by two examples. The gray areas in Fig. 11 indicate the estimated ranges of active concentration of heavy metals in uncontaminated lands. Finally, based on the environmental quality concern, the HC$_5$ was then derived and was served as the reference value of a certain heavy metal (total concentration). The reference value may be adjusted according to the variations of total concentration of heavy metals in soils and their regarded PAFs. Based on Netherland’s strategy, 95% of the eco-toxicity of a certain heavy metal was assured to be controlled by the reference value.

**Fig. 10.** Two examples of the relationships between the concentrations of metal elements ((a) Cu and (b) Zn) and Al$_2$O$_3$ in the topsoil (symbol "x") and the subsoil (symbol "+") in the Netherland (Mol et al., 2012).
2.3 Human health risk assessment

There is an increasing use of risk-oriented policies to deal with the local effects of heavy metals in foods and also in the soil environment (Laio and Ling, 2003; Ma et al., 2007). A specific objective underlying the UK government’s approach method to land contamination is to identify and remove unacceptable risks to human health and the environment (DEFRA of UK, 2012). Environmental risk assessment is a key element in appraisal so that decisions can be made on equitable policy and other factors. In UK, the contaminated land is identified based on risk assessment. Part II of the Department of the Environment Transport and the Regions section of the Environmental Protection Act, specifies that the source-pathway-receptor linkage concept for risk assessment is carried out to assess the risk of contaminated lands. The objective is to ensure the land is fit for either its current use or redevelopment. All three elements of the linkage must be present for a risk to exist. If any of the elements of a pollutant linkage is absent, there can be no risk and the land is deemed uncontaminated.

The human health risk assessment was also used to establish the regulatory soil limit in many countries (Carlon, 2007). The aim is to ensure the human health risks below an acceptable level. The exposure pathways mainly includes direct intake of heavy metals via oral injection, dermal injection, and inhalation of soils. Because of the complicity of the indirect human risk posed from edible crops, the food safety assessment can be conducted as an alternative. The limit level in edible crops can be estimated followed by the estimation of soil limit levels with the relationship of the concentration of metals in soil and in plants.

2.4 Metal concentrations in edible agro-productions

In the approaches of human health risk assessment for normal land, the exposure pathways of heavy metals are generally designated as the exposure from soils which can be the oral and dermal soil intake and soil inhalation (Su and Chen, 2009; Lai et al., 2010; Su et al., 2014). In the rural land, the risks of heavy metal in food crops can be evaluated (Khan et al., 2008). Because edible crops may be produced which may accumulate high levels of heavy metals before un-ignorable risks are posed via direct injection of soils, the hazardous evaluation of human health related to food chain can be critical. The dose effect of food metal content on human health can be estimated. Thus the limits of per capital intake of certain metal elements can be identified. With an average intake amount of a certain food (rice or vegetables), the limit of metal concentrations of this food can be calculated. According to the relationships between metal concentration of crop tissues and in soils as discussed in session 2.1, the soil limits can be obtained consequently using the soil-plant translocation factors. Finally, to ensure human health safety, the value, which is lower, of the soil heavy metal limits derived from risk assessment or hazardous evaluation of food web should be preferentially concerned as a regulatory standard (Su and Chen, 2009; Lai et al., 2010; Su et al., 2014)
2.5 Social and economic resources

The economic and executive resources are precious and often limited, and thus strict regulations or captious limit levels probably result in waste of these resources, decreases in the efficiency of soil pollution management, and may restrict the social/economic development. Therefore, in order to formulate the relative regulations and limit levels of heavy metals, an integrated concern as described above should be conducted to counterpoise the scientific, technologic, economic, and social factors. Moreover, the regulations and limit levels should be able to be revised to accommodate environment and social changes and to provide the maximum efficiency of total resources with the premise of safety of human beings.

3. Regulation development of heavy metals in soils of Taiwan

The background levels of heavy metals in soils of Taiwan were shown in Table 1. Because of the complexity of Taiwan’s geological condition, the background levels of several metal elements are in a wide range. The high background levels may caused by pedogenic processes in Taiwan. The mean background level of Cd is 1.78 mg/kg while the background limit is 3 mg/kg which are even higher than the pollution limit in several countries (0.3 mg/kg in Denmark and 1.4 mg/kg for rural soils in Canada). Some geological enrichment Cd is often occurred to be less mobile and available. Accordingly, it is not reasonable to set the regulatory limit of soil Cd at a low concentration.

Table 1. The distribution of heavy metals in uncontaminated soils in Taiwan (mg/kg)

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>8.50</td>
<td>1.78</td>
<td>40.4</td>
<td>20.4</td>
<td>0.13</td>
<td>40.5</td>
<td>30.5</td>
<td>171</td>
</tr>
<tr>
<td>Range</td>
<td>2.6-18.9</td>
<td>N.D-3.1</td>
<td>22.9-98.8</td>
<td>7.2-35.1</td>
<td>N.D-1.6</td>
<td>18.6-66.7</td>
<td>N.D-127</td>
<td>37-392</td>
</tr>
<tr>
<td>Background upper limit</td>
<td>18.0</td>
<td>3.0</td>
<td>100</td>
<td>35</td>
<td>0.5</td>
<td>60</td>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

(Chen and Lee, 1995)

The present heavy metal regulation in rural soil and food safety were shown in Table 2. The food regulations were set up based on health risk assessments and only for Cd, Hg, and Pb. The present regulation of heavy metals in soil might be inaccurate for human health protection since more evidences and local parameters in risk assessments are provided in Taiwan. In addition, the social and economic conditions, the industrial development and executive resources changed a lot within last 14 years. Therefore, the revisions of Taiwan’s regulatory standards (i.e. SPCS and SPMS) with an integrated evaluation need to be conducted with immediate attentions.

Table 2. The present heavy metal regulation in soil and food safety in Taiwan

<table>
<thead>
<tr>
<th>Element</th>
<th>Rural soil (mg/kg)</th>
<th>Food safety level (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPCS</td>
<td>SPMS</td>
</tr>
<tr>
<td>As</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>Cd</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>Cr</td>
<td>250</td>
<td>175</td>
</tr>
<tr>
<td>Cu</td>
<td>200</td>
<td>120</td>
</tr>
<tr>
<td>Hg</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Ni</td>
<td>200</td>
<td>130</td>
</tr>
<tr>
<td>Pb</td>
<td>500</td>
<td>300</td>
</tr>
<tr>
<td>Zn</td>
<td>600</td>
<td>260</td>
</tr>
</tbody>
</table>

SPCS: Soil Pollution Control Standard; SPMS: Soil Pollution Monitoring Standard. -: No regulation
4. Health risk-based approaches of standard revisions in Taiwan

According to the SGWPR Act of Taiwan for a control site, a control project must be conducted to decrease the health risk of contaminants to an acceptable level. At a remediation site, a health risk assessment can be first calculated by the pollution producer. The huge costs incurred by remediation sites during the remediation process can be reduced if the risk of exposure is controlled by suitable practices. When the concentrations of contaminants of the remediation site was reduced to below the SPCS is not possible because of the limitation of geologic conditions, site characteristics of the contaminant, or the remediation techniques, risk assessment be carried out with the provision of a flexible remediation target. In addition, if the pollution producer is not identified, Taiwan EPA can consider the financial and environmental factors in processing a risk assessment of the contaminated site. Lai et al. (2010) assessed the human health risks of metal-contaminated sites in Taiwan using several risk assessment models and also revealed the efficiency of remediation approaches on risk reductions.

To establish the regulatory standards or limit levels of heavy metals in soils using the health risk-based approach becomes a major method in the world. Because the risk assessment may be inaccurate when Taiwan’s regulatory limits were set referring to the approaches abroad and more and more local soil and environmental parameters are provided, revise of the SPCSs and SPMSs in Taiwan needs to involve the latest results of human risk assessment.

In the health risk assessment of heavy metals in different land use types, the main exposure pathways of soil heavy metals were considered to include (1) oral intake of the soil, (2) dermal absorption of the soil, and (3) inhalation of the soil. The receptor was set to be adult and child individually and the selection of pathways was depended on the metal elements. Even a small fraction of Cr (III) oxidation to chromate in soils may be sufficient to contaminate groundwater (Chung et al., 2001). Therefore, the pathways of oral intake and dermal absorption of groundwater were involved for Cr (VI) risk assessment. For Hg risk assessment, inhalation intake of Hg vapors from surface soil (0-15 cm depth) and subsoil (15-30 cm depth) were also involved as an exposure pathway. Parameters used worldwide were adapted referring to international researches and several local parameters, which had been proposed from local researches.

4.1 Regulation of heavy metals in different land uses of Taiwan

The exposure pathway of heavy metals to human and concerns of economic development may be quite different among types of land uses. One target value for soil pollution management might be too inflexible and unfavorable for brown field development. Remediation of contaminated sites is costly, and thus it is not economic efficient to take all the contaminated sites into remediation approaches according to the one target value of heavy metal concentration in soils regardless of land use types. For example, industrial park areas may have high probability of heavy metals enrichment in soils but may provide lower exposure frequency to human than other land uses. The risks assessment for the receptor of child is excluded. Therefore, the limit level of soil heavy metals in industrial park areas should be set higher value than other land uses according to health risk assessment. Carlon (2007) also denoted the different set of exposure pathways for different land uses. Besides health risks, a rural land should be more concerned about the crop productivity, crop toxicity and food safety than other land uses. In rural soils, the lowest limit level of those for health risk control, food safety assurance and crop yield maintenance should be taken as the ultimate regulatory standard. With the premise of protection of health risk and food safety, the higher acceptable yield reduction can be used according to the economic development, the executive resources limit, and the higher regulatory standard will be obtained. Therefore, we should establish a more flexible framework to manage our soil pollution sites in different land uses. The different types of land uses should be categorized, the more efficiency of soil resources can be derived. However, it should be announced that complicated zoning soil system could result in the difficulty of comprehension and execution of the regulations.

According to the risk assessment results in different land uses of Taiwan shown in Table 3, the suggested risk-based approached regulation of As and Pb for both industrial park soil and normal land were much lower than the present regulation of SPCSs. Therefore, the present SPCSs of As and Pb should be revised to decrease a lower value. In contrary, the suggested risk-based approached regulation of Cd, Cu, Hg, Ni, Zn and Cr(III) were higher than the present regulation of SPCSs which should be revised to appropriately increase higher values. The risk-based approached regulation of
Cr(VI) were much lower than that of Cr(III). Therefore, a new SPCSs of Cr(VI) is strongly recommended. Generally, the suggested risk-based approached regulation of heavy metals in industrial park should be roughly estimated as at least 2 times to 5 times higher than those for normal land, based on the regulations of metals in other countries.

Table 3. The present regulatory control standards of heavy metals in soils (rural soil and general soil) and calculated health risk-based approached regulations of heavy metals in normal land and industrial park in Taiwan

<table>
<thead>
<tr>
<th>Metal element</th>
<th>Present SPCS (mg/kg)</th>
<th>Calculated risk-based approached regulations (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Normal land</td>
<td>Industrial park</td>
</tr>
<tr>
<td>As</td>
<td>60</td>
<td>0.6</td>
</tr>
<tr>
<td>Cd</td>
<td>20 (5)</td>
<td>40</td>
</tr>
<tr>
<td>Cr</td>
<td>Total: 250</td>
<td>Cr (III): 127,000 Cr (III): 920,000</td>
</tr>
<tr>
<td>Cu</td>
<td>400 (200)</td>
<td>85-850</td>
</tr>
<tr>
<td>Hg</td>
<td>20 (5)</td>
<td>20</td>
</tr>
<tr>
<td>Ni</td>
<td>200</td>
<td>1,300</td>
</tr>
<tr>
<td>Pb</td>
<td>2,000 (500)</td>
<td>130</td>
</tr>
<tr>
<td>Zn</td>
<td>2,000 (600)</td>
<td>25,000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Industrial park</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (VI): 6</td>
<td></td>
</tr>
<tr>
<td>Cr (VI): 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>615-6,150</td>
</tr>
</tbody>
</table>

¶: Values in the parentheses are the control standards for rural soils. SPCS: Soil Pollution Control Standards.

4.2 Suggested revision of arsenic (As) control standard
Arsenic (As) is confirmed to be one of the carcinogen elements and was categorized as Group A carcinogen based on IRIS Classification and as Group 1 based on IARC Classification. As shown in Table 4, the suggested risk-based approached regulation of As was 0.6 and 1.6 mg/kg for normal land and industrial park, respectively. Therefore, the stricter limit levels were suggested. In Taiwan, As is not listed in the food quality standards and the related parameters of soil-plant transportation of As is insufficient. As is easily to be retained by soils and edible parts of crops commonly contained low level of As. Consequently, the revision of As SPCSs was established only based on health risk assessment from now. However, the soil background level of As is 8-15 mg/kg with an estimated background level of 18 mg/kg (Table 1), which is higher than the health baselines of As. Consequently, it is not reasonable to set the As SPCSs based on the health baselines, 0.6 and 1.6 mg/kg for normal land and industrial park. For an expedient management strategy, the stricter levels of 30 and 24 mg/kg were suggested to be set up as arsenic SPCS and SPMS for rural land and normal land, respectively. It was also suggested to add the total As SPCS and SPMS at 60 and 30 mg/kg for industrial park area, respectively. Arsenic total content, As speciation and soil characteristics played a major role in determining As solubility and human health posed by rice consumption (Juhasz et al., 2006; Su and Chen, 2010a, 2010b, 2010c, 2012; Su et al., 2014a, 2014b). Therefore, soil cultivation management that can transform As to As (III), As(V) or DMA with low availability and toxicity in soils and brown rice in different soil conditions. For example, the different soil water management, such as aerobic treatment (drainage), can reduce total As concentration in soil solution and consequent reduce the As uptake in the brown rice of As-contaminated soils in Taiwan (Huang et al., 2013a, 2013b, 2014).

Table 4. The risk assessment results calculated from health risk-based regulation of As in Taiwan

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline (mg/kg)</th>
<th>Cancer risk from soil exposure</th>
<th>Total cancer risk</th>
<th>Hazard quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adult</td>
<td>Yes</td>
<td>0.6</td>
<td>4.48E-07, 1.99E-12, 3.25E-08</td>
<td>4.80E-07, 3.24E-03, 1.08E-10</td>
<td>2.36E-04, 3.48E-03</td>
</tr>
<tr>
<td>Child</td>
<td></td>
<td>8.12E-07, 1.47E-12, 5.56E-08</td>
<td>8.68E-07, 2.35E-02, 3.18E-10</td>
<td>1.61E-03, 2.51E-02</td>
<td></td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td>8.89E-07, 3.95E-12, 6.46E-08</td>
<td>9.53E-07, 8.65E-03, 2.88E-10</td>
<td>6.28E-04, 9.29E-03</td>
<td></td>
</tr>
</tbody>
</table>
4.3 Suggested revision of cadmium (Cd) control standard

Cd has limited evidence to be one of the carcinogen elements and was categorized as Group B1 carcinogen based on IRIS Classification. As shown in Table 5, the suggested risk-based approached baseline was 40 and 290 mg/kg for normal land and industrial park, respectively. The values are much higher than the present SPCSs. Therefore, higher limit values might be taken. The provisional tolerable monthly intake (PTMI) of 25 μg Cd/kg body is suggested by WHO. Conservatively estimating that 40% of the total Cd intake is contributed by rice consumptions, the food quality standard of Cd in rice was then estimated to be 0.4 mg/kg. Furthermore, the soil-rice transportation factor of Cd was determined as 104% and consequently, the soil Cd regulation based on the food safety can be calculated as 0.38 mg/kg. The phytotoxicity effect of Cd was not obvious at such a low Cd level in soils which indicated that Cd may be easily involved into food chain and with high risks to human health. From the integrated assessment, food safety should be the critical concern to establish soil Cd in SPCSs.

The level of soil Cd is up to 1.78 mg/kg in average with a suggested background level of 3 mg/kg because of different geological formation and factors. The suggested SPCS of Cd based on food safety is even lower than that of background value. This indicates that proposed Cd SPCSs for rural land upon food safety is unfeasible. Fig. 12 shows the uncertainty of the relationships between Cd concentration of rice grain and soils in Taiwan (Su et al., 2009; Hseu et al., 2010). It indicates that there were other factors to control the Cd uptake in different rice variety grown in different soil characteristics of Cd-contaminated soils. Therefore, in order to develop the techniques of cultivation management to decrease Cd uptake by rice might be an efficient strategy to ensure the food safety. For example, soil Cd availability of soils decreased with lime application rates in acidic soils and also with anaerobic condition under sulfur-enriched Cd-contaminated soils. Based on the integrated assessment, only the SPMS of rural land was suggested to be revised. It was suggested the Cd SPCS can be set up as 100 and 50 mg/kg for the industrial park areas, respectively.

Table 5. The risk assessment results calculated from suggested health baseline of Cd in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline (mg/kg)</th>
<th>Cancer risk from soil exposure</th>
<th>Total cancer risk</th>
<th>Hazard quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oral</td>
<td>Inhalation</td>
<td>Dermal</td>
</tr>
<tr>
<td>Adult</td>
<td>Yes</td>
<td>40</td>
<td>5.56E-11</td>
<td>5.56E-11</td>
<td>1.30E-01</td>
</tr>
<tr>
<td>Child</td>
<td></td>
<td>290</td>
<td>3.00E-10</td>
<td>3.00E-10</td>
<td>9.40E-01</td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td>290</td>
<td>3.00E-10</td>
<td>3.00E-10</td>
<td>9.40E-01</td>
</tr>
</tbody>
</table>

Fig. 12. The relationship between Cd concentration in brown rice and extractable concentration of Cd in soils of Taiwan. (a) low Cd-contaminated soils; (b) high Cd-contaminated soils. (Hseu et al., 2010)
Although it is difficult to ensure food safety by control the total Cd level in soils, Römkens et al. (2009) showed a good prediction model for Cd uptake by brown rice of Taiwan using several soil-plant transfer models and denoted that CaCl₂ extractable Cd and Zn content in soils can be good indicators to predict the Cd concentration in brown rice (Fig. 13). Since food safety is the critical consideration of Cd-polluted soils, this approach might be used to establish the regulatory standards of soil Cd, which implicated that the pollution management using available Cd level might be more feasible and efficient than using the total Cd level. This concept of availability management of Cd should be referred for the revisions. Carlon (2007) also listed the countries which use extractable level of metals as regulatory guidance limits (Germany, Japan and UK).

![Fig. 13. Measured versus predicted levels of Cd in brown rice for the first harvest and the second harvest in Taiwan (Römkens et al., 2009).](image)

Table 6. Soil regulation of Cd based on risk assessment of food safety.

<table>
<thead>
<tr>
<th>Element</th>
<th>Provisional tolerable monthly intake (μg kg⁻¹)</th>
<th>Intake fraction from rice (%)</th>
<th>Per capita daily rice consumption (g day⁻¹)</th>
<th>Average body weight (kg)</th>
<th>Estimated rice metal limit (mg kg⁻¹)</th>
<th>Soil-rice transportation factor (%)</th>
<th>Estimated soil metal level regarded to rice metal limit (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>25</td>
<td>40</td>
<td>170</td>
<td>60</td>
<td>0.4</td>
<td>104</td>
<td>0.38</td>
</tr>
</tbody>
</table>

4.4 Suggested revision of Hg control standard

Mercury (Hg) was categorized as Group 3 by IARC classification and as Group D by IRIS classification, which indicated that Hg was not a carcinogen. The results of health risk assessment were shown in Table 7. Besides the direct intake of soils, inhalation of Hg vapor from topsoil and subsoil was also involved in the risk assessment. The suggested health baseline of Hg in soils was 20 and 170 mg/kg for normal land and industrial park, respectively. The Hg limit level of brown rice was set up as 0.05 mg/kg in Taiwan. There is no sufficient information on the relationship between Hg concentration in crop and in soils. Hg is easily to be retained by soils and edible parts of crops commonly contained low level of Hg. Consequently, the revision of Hg SPCSs was established only based on health risk assessment for new version. The Hg level in soils shown in Table 1 is less than 1.6 mg/kg with a suggested background level of 0.5 mg/kg. Therefore, the present SPCSs and SPMSs of Hg for normal land and rural land were preserved. It was also suggested to add the new SPCS and SPMS as 100 and 50 mg/kg for the industrial park area, respectively.
Table 7. The risk assessment results calculated from suggested health baseline of Hg in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline (mg/kg)</th>
<th>Hazard quotient</th>
<th>Total hazard quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oral and Inhalation (soil)</td>
<td>Dermal</td>
<td></td>
</tr>
<tr>
<td>Adult</td>
<td>No</td>
<td>20</td>
<td>1.08E-01</td>
<td>1.68E-07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.71E-02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.65E-01</td>
</tr>
<tr>
<td>Child</td>
<td></td>
<td>7.84E-01</td>
<td>4.95E-07</td>
<td>1.69E-01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.53E-01</td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td>170</td>
<td>9.19E-01</td>
<td>1.43E-06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.86E-02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.87E-01</td>
</tr>
</tbody>
</table>

4.5 Suggested revision of Cu control standard

Cu is not a carcinogen and was categorized as Group D by IRIS classification while it was not listed in IARC classification. The results of health risk assessment for soil Cu are shown in Table 8. The suggested health baselines of soil Cu in normal land and in industrial park were estimated as 850 and 6,150 mg/kg, respectively. The values were much higher than the present SPCSs. Therefore, higher limit values might be proposed. The provisional tolerable daily intake (PTDI) of 500 μg Cd/kg body and the provisional tolerable weekly intake (PTWI) of 3,500 μg Cu/kg body were suggested by WHO. Conservatively estimating that 40% of the total Cu intake is contributed by rice consumptions, the food quality standard of Cu in rice was then estimated to be 70.6 mg/kg (Table 9). Furthermore, the soil-rice transportation factor of Cu was determined as 8.87% and consequently, the soil Cu limit based on food safety can be calculated as 795 mg/kg.

Concerning about the phytotoxicity, unacceptable yield drops (50%) occurred when Cu concentration in soils reached to about 600 mg/kg in Taiwan. Moreover, Cu accumulation in brown rice reached to a plateau at approximately 15 mg/kg with increasing soil Cu available concentration in soils (up to 400 mg/kg) in Taiwan (Fig. 14) (Guo et al., 2014). This physiological limitation results in ignore hazard to the food safety. Comparing the soil control standard calculated from risk assessment, food safety evaluation and the phytotoxicity of Cu, the crop yields drops should be the critical concern for soil control standard. In addition, the soil level of Cu was 20 mg/kg in average with the estimated background of 35 mg/kg (Table 1), which are much lower than the control standard as described above. Although the risk-based regulation of soil Cu can be as a much higher value, the present SPCSs of Cu were kept at 200 mg/kg to be preserved for more communication. For rural land, the SPCS of Cu was suggested to be kept at present value 200 mg/kg or to be increased to 400 mg/kg with the same risk compared with the present SPCS 200 mg/kg, as well as that for normal land (Guo et al., 2014). It was also suggested to add the new SPCS and SPMS of soil Cu at 2,000 and 1,000 mg/kg for the industrial park area, respectively.

Table 8. The risk assessment results calculated from suggested health baseline of Cu in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline (mg/kg)</th>
<th>Cancer risk from soil exposure</th>
<th>Total cancer risk</th>
<th>Hazard quotient</th>
<th>Total hazard quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oral and Inhalation (soil)</td>
<td>Dermal</td>
<td></td>
<td>Oral</td>
<td>Inhilation</td>
</tr>
<tr>
<td>Adult</td>
<td>No</td>
<td>850</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Child</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td>6,150</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9. Soil regulation of Cu based on assessment of food safety

<table>
<thead>
<tr>
<th>Element</th>
<th>Provisional tolerable weekly intake (μg kg⁻¹)</th>
<th>Intake fraction from rice (%)</th>
<th>Per capita daily rice consumption (g day⁻¹)</th>
<th>Average body weight (kg)</th>
<th>Estimated rice metal limit (mg kg⁻¹)</th>
<th>Soil-rice transportation factor (%)</th>
<th>Estimated soil metal level regarded to rice metal limit (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>3,500</td>
<td>40</td>
<td>170</td>
<td>60</td>
<td>70.6</td>
<td>8.87</td>
<td>795</td>
</tr>
</tbody>
</table>

135
4.6 Suggested revision of Zn control standard

Zn is not a carcinogen and was categorized as Group D by IRIS classification while it was not listed in IARC classification. The results of health risk assessment for soil Zn are shown in Table 10. The suggested health baselines of soil Zn in normal land and in industrial park were estimated to be 25,000 and 185,000 mg/kg, respectively. The values are much higher than the present SPCSs. Therefore, higher control standard value might be proposed. The PTDI of 500 μg Zn/kg body and the PTWI of 7,000 μg Zn/kg body were suggested by WHO. Conservatively estimating that 40% of the total Zn intake is contributed by rice consumptions, and the food quality standard of Zn in rice was then estimated as 141 mg/kg (Table 11). Furthermore, the soil-rice transportation factor of Zn was determined to be 15% and consequently, the soil Zn limit based on food safety can be calculated as 940 mg/kg. Concerning about the phytotoxicity, unacceptable yield drops (50%) occurred when Zn concentration in soils reached to 500-800 mg/kg in Taiwan. Moreover, Zn accumulation in rice reached to a plateau at approximately 60 mg/kg with increasing Zn available concentration in soils in Taiwan (Fig. 15) (Guo et al., 2014). This physiological limitation results in ignorable hazard to the food safety. Comparing the soil limit values derived from risk assessment, food safety evaluation and the phytotoxicity of Zn, the yields drops should be the critical concern for soil standard establishment. In addition, the soil level of Zn was 171 mg/kg in average with the estimated background limit of 120 mg/kg (Table 1) which are much lower than the limit levels as described above. Although the risk-based limit of Zn can be much higher, the present SPCSs of Zn were suggested to be preserved for social communication. For rural land, the SPCS of Zn were suggested to be kept at 600 mg/kg or increased to 900 mg/kg, respectively. It was suggested not to set the Zn limit level in soils for the industrial park areas as well as the regulations of Germany, France, and Belgium.

Table 10. The risk assessment results calculated from suggested health baseline of Zn in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline (mg/kg)</th>
<th>Cancer risk from soil exposure</th>
<th>Total cancer risk</th>
<th>Hazard quotient</th>
<th>Total hazard quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oral</td>
<td>Dermal</td>
<td>Oral</td>
<td>Inhalation</td>
</tr>
<tr>
<td>Adult</td>
<td>No</td>
<td>25,000</td>
<td>—</td>
<td>—</td>
<td>1.35E-01</td>
<td>—</td>
</tr>
<tr>
<td>Child</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>9.80E-01</td>
<td>9.80E-01</td>
</tr>
<tr>
<td>Industrial park</td>
<td>185,000</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.00E+00</td>
<td>—</td>
</tr>
</tbody>
</table>
Table 11. Soil regulation of Zn based on assessment of food safety

<table>
<thead>
<tr>
<th>Element</th>
<th>Provisional tolerable weekly intake ( (\mu g \ kg^{-1}) )</th>
<th>Intake fraction from rice ( (%) )</th>
<th>Per capita daily rice consumption ( (g \ day^{-1}) )</th>
<th>Average body weight ( (kg) )</th>
<th>Estimated rice metal limit ( (mg \ kg^{-1}) )</th>
<th>Soil-rice transportation factor ( (%) )</th>
<th>Estimated soil metal level regarded to rice metal limit ( (mg \ kg^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>7,000</td>
<td>40</td>
<td>170</td>
<td>60</td>
<td>141</td>
<td>15.0</td>
<td>940</td>
</tr>
</tbody>
</table>

Fig. 15. The relationship between Zn concentration in brown rice and availability content of Zn in soils of Taiwan \((n=2135)\). The estimated limit level of Zn in brown rice is 141 mg/kg. (TARI, 2008a, 2008b, 2010 and 2012)

4.7 Suggested revision of Ni control standard

Ni is confirmed to be one of the carcinogen elements and was categorized as Group A carcinogen based on IRIS Classification and as Group 1 based on IARC Classification. The results of health risk assessment for soil Ni are shown in Table 12. The suggested health baselines of soil Ni in normal land and in industrial park were estimated as 1,300 and 9,500 mg/kg, respectively. The values were much higher than the present SPCGs. Therefore, higher limit values might be proposed. The PTWI of 35 \( \mu g \) Ni/kg were suggested by WHO. Conservatively estimating that 40% of the total Ni intake is contributed by rice consumptions, the food quality standard of Ni in brown rice was then estimated to be 0.7 mg/kg (Table 13). However, recent researches suggested the Ni limit level of 9 mg/kg in brown rice which may not pose health risks to most of people. Furthermore, the soil-rice transportation factor of Ni was determined to be 5.72% and consequently, the soil Ni limit based on food safety can be calculated as 157 mg/kg. The soil level of Ni was 45 mg/kg in average with the estimated background limit of 60 mg/kg (Table 1). Comparing the soil limit values derived from risk assessment, food safety evaluation and the phytotoxicity of Ni, the food safety should be the critical concern for soil standard establishment for rural land.

Table 12. The risk assessment results calculated from suggested health baseline of Ni in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline ( (mg/kg) )</th>
<th>Cancer risk from soil exposure</th>
<th>Total cancer risk</th>
<th>Hazard quotient</th>
<th>Total hazard quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oral Inhalation Dermal</td>
<td>Oral Inhalation Dermal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adult</td>
<td>Yes</td>
<td>1,300</td>
<td>2.41E-10 2.41E-10</td>
<td>2.41E-10 1.05E-01 3.64E-05</td>
<td>3.19E-02</td>
<td>1.37E-01</td>
</tr>
<tr>
<td>Child</td>
<td></td>
<td></td>
<td>1.78E-10 1.78E-10</td>
<td>1.78E-10 7.65E-01 1.07E-04</td>
<td>2.18E-01</td>
<td>9.83E-01</td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td>9,500</td>
<td>1.31E-09 1.31E-09</td>
<td>1.31E-09 7.70E-01 2.66E-04</td>
<td>2.33E-01</td>
<td>1.00E+00</td>
</tr>
</tbody>
</table>
Table 13. Soil regulation of Ni based on assessment of food safety

<table>
<thead>
<tr>
<th>Element</th>
<th>Provisional tolerable weekly intake (μg kg⁻¹)</th>
<th>Intake fraction from rice (%)</th>
<th>Per capita daily rice consumption (g day⁻¹)</th>
<th>Average body weight (kg)</th>
<th>Estimated rice metal limit (mg kg⁻¹)</th>
<th>Soil-rice transportation factor (%)</th>
<th>Estimated soil metal level regarded to rice metal limit (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>35</td>
<td>40</td>
<td>170</td>
<td>60</td>
<td>0.7 to 9</td>
<td>5.72</td>
<td>157</td>
</tr>
</tbody>
</table>

Although the risk-based limit of Ni can be much higher, the present SPCSs and SPMSs of Ni were suggested to be preserved for social acceptance. For rural land, the SPCS and SPMS of Zn were also preserved. Furthermore, it was suggested to add the new SPCS and SPMS of Ni at 1,000 and 500 mg/kg, respectively for the industrial park areas.

4.8 Suggested revision of Pb control standard

Pb was categorized as Group B2 by IRIS classification and was a probable human carcinogen. As shown in Table 14, the suggested health baseline with acceptable health risks was 130 and 318 mg/kg for normal land and industrial park, respectively. These values are much lower than present SPCSs and SPMSs of Pb. Therefore, stricter limit levels were proposed. The food quality standard of Pb in brown rice was estimated as 0.2 mg/kg in Taiwan (Table 15). Furthermore, the soil-rice transportation factor of Pb was determined as 0.55% and consequently, the soil Pb limit based on food safety can be calculated as 36.3 mg/kg. Pb is easily retained by soils and thus its availability is low. Generally, Pb accumulation in edible part of crops was found to be much lower than that of the root. The phytotoxicity effect of Pb was also un-obvious at this soil level. From the integrated assessment, risk assessment should be the critical concern to establish new Pb SPCSs and SPMSs. The soil level of Pb was 30.5 mg/kg in average with the estimated background level of 120 mg/kg (Table 1). Therefore, the present SPCSs and SPMSs of Pb for normal land and rural land were suggested to be lowered down to 150 and 120 mg/kg, respectively. It was also suggested to add new SPCS and SPMS of Pb at 300 and 150 mg/kg for the industrial park area, respectively.

Table 14. The risk assessment results calculated from suggested health baseline of Pb in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline (mg/kg)</th>
<th>Cancer risk from soil exposure</th>
<th>Total cancer risk</th>
<th>Hazard quotient</th>
<th>Total hazard quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oral  Inhalation Dermal</td>
<td></td>
<td>Oral  Inhalation Dermal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adult</td>
<td>Yes</td>
<td>130</td>
<td>5.50E-07 1.20E-12</td>
<td>5.50E-07</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td>318</td>
<td>1.00E-06 2.19E-12</td>
<td>—</td>
<td>1.00E-06</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 15. Soil regulation of Pb based on assessment of food safety

<table>
<thead>
<tr>
<th>Element</th>
<th>Provisional tolerable weekly intake (μg kg⁻¹)</th>
<th>Intake fraction from rice (%)</th>
<th>Per capita daily rice consumption (g day⁻¹)</th>
<th>Average body weight (kg)</th>
<th>Estimated rice metal limit (mg kg⁻¹)</th>
<th>Soil-rice transportation factor (%)</th>
<th>Estimated soil metal level regarded to rice metal limit (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>—</td>
<td>40</td>
<td>170</td>
<td>60</td>
<td>0.2</td>
<td>0.55</td>
<td>36.3</td>
</tr>
</tbody>
</table>
4.9 Suggested revision of Cr control standard

Cr can pose risks in quite different ways among its species. Cr(VI) is a carcinogen and was categorized as Group A in IRIS classification while Cr(III) is not classified for carcinogen in the Group D. To efficiently managing Cr pollution of soils, adding the new SPCSs and SPMS of Cr(VI) is strongly recommended. According to the risk assessment, the health baseline of soil Cr(III) for normal land and industrial park were 127,000 and 920,000 mg/kg, respectively (Table 16). The values were very much higher than the present SPCSs. Therefore, higher limit values might be taken in the suggested revision.

Besides the pathways of direct soil intake, two groundwater intake pathways were also involved in the risk assessment of Cr(VI) which are oral and dermal exposure of groundwater (Table 17 and Table 18). In contrarily with Cr(III), the health risk assessment of Cr(VI) suggested that the health baselines of soil Cr(VI) were only 6 and 10 mg/kg for normal land and industrial park, respectively. Cr in rice is not listed in the food quality standard in Taiwan. Referring to WHO’s suggestion, the PTDI of 3.3 μg Cr/kg or the PTWI of 23.3 μg Cr/kg were used. Conservatively estimating that 40% of the total Cr intake is contributed by rice consumptions, the food quality standard of Cr in rice was then estimated to be 0.47 mg/kg (Table 19). Furthermore, the soil-rice transportation factor of Cr was determined to be 0.52% and consequently, the soil Cr limit based on food safety can be calculated as 90.4 mg/kg. This level is lower than the present SPCSs of Cr. The estimated soil limit of Cr based on food safety might not consider the significant differences in the toxicity among Cr species. In a soil environment, Cr(VI) is easily reduced and transformed into Cr(III) which is less mobile and less available to crops. In crops, Cr is accumulated mainly in roots and its transportation to shoots was less obvious (Hseu and Iizuka, 2013). Except for the soils weathered from Serpentinite which geological content with high levels of Cr, the soil level of Cr is approximately 40 mg/kg in average with the estimated background limit of 100 mg/kg (Table 1).

Although the acceptable health baseline of Cr(III) was estimated to be much higher value, the SPCS and SPMS for rural land were not suggested to be raised because of the uncertainty of Cr(III) hazard to food chain. The SPCS and SPMS of Cr(III) for normal land were suggested to be revised to 1,000 and 550 mg/kg, respectively. In addition, because of the high health risks of Cr(VI), addition of soil limit of Cr(VI) SPCSs and SPMSs was strongly recommended. For normal land, the CPCS and SPMS were suggested to be 10 and 5 mg/kg while those for industrial park were suggested to be 20 and 10 mg/kg, respectively.

### Table 16. The risk assessment results calculated from suggested health baseline of Cr(III) in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline (mg/kg)</th>
<th>Cancer risk from soil exposure</th>
<th>Total cancer risk</th>
<th>Hazard quotient</th>
<th>Total hazard quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oral</td>
<td>Inhalation</td>
<td>Dermal</td>
<td>Oral</td>
</tr>
<tr>
<td>Adult</td>
<td>No</td>
<td>127,000</td>
<td></td>
<td></td>
<td></td>
<td>1.37E-01</td>
</tr>
<tr>
<td>Child</td>
<td></td>
<td>920,000</td>
<td></td>
<td></td>
<td></td>
<td>9.96E-01</td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.95E-01</td>
</tr>
</tbody>
</table>

### Table 17. The cancer risk assessment results calculated from suggested health baseline of Cr(VI) in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th>Suggested Health Baseline (mg/kg)</th>
<th>Cancer risk from soil and groundwater exposure</th>
<th>Total Cancer Risk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oral (soil)</td>
<td>Inhalation (soil)</td>
</tr>
<tr>
<td>Adult</td>
<td>Yes</td>
<td>6</td>
<td>3.89E-10</td>
<td></td>
</tr>
<tr>
<td>Child</td>
<td></td>
<td></td>
<td>2.87E-10</td>
<td></td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td>10</td>
<td>4.83E-10</td>
<td></td>
</tr>
</tbody>
</table>
Table 18. The hazard quotient calculated from suggested health baseline of Cr(VI) in Taiwan.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Carcinogen</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Suggested</td>
<td>Hazard</td>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Health</td>
<td>quotient</td>
<td>hazard quotient</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Baseline</td>
<td>Oral (soil)</td>
<td>Inhalation</td>
<td>Dermal (soil)</td>
<td>Oral (groundwater)</td>
<td>Dermal (groundwater)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(mg/kg)</td>
<td>Oral (soil)</td>
<td>Inhalation (soil)</td>
<td>Dermal (soil)</td>
<td>Oral (groundwater)</td>
<td>Dermal (groundwater)</td>
<td></td>
</tr>
<tr>
<td>Adult</td>
<td>Yes</td>
<td>6</td>
<td>3.24E-03</td>
<td>1.51E-07</td>
<td>—</td>
<td>4.45E-01</td>
<td>1.03E-01</td>
</tr>
<tr>
<td>Child</td>
<td></td>
<td>2.35E-02</td>
<td>4.46E-07</td>
<td>—</td>
<td>7.00E-01</td>
<td>2.46E-01</td>
<td>9.69E-01</td>
</tr>
<tr>
<td>Industrial park</td>
<td></td>
<td>10</td>
<td>5.41E-03</td>
<td>2.52E-07</td>
<td>—</td>
<td>7.42E-01</td>
<td>1.71E-01</td>
</tr>
</tbody>
</table>

Table 19. Soil regulation of total Cr based on assessment of food safety.

<table>
<thead>
<tr>
<th>Element</th>
<th>Provisional tolerable weekly intake (μg kg⁻¹)</th>
<th>Intake fraction from rice (%)</th>
<th>Per capita daily rice consumption (g day⁻¹)</th>
<th>Average body weight (kg)</th>
<th>Estimated rice metal limit (mg kg⁻¹)</th>
<th>Soil-rice transportation factor (%)</th>
<th>Estimated soil metal level regarded to rice metal limit (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>23.3</td>
<td>40</td>
<td>170</td>
<td>60</td>
<td>0.47</td>
<td>0.52</td>
<td>90.4</td>
</tr>
</tbody>
</table>

5. Summary

The strategy for soil pollution control, remediation and restoration is being revised based on risk assessments looking after both sides of environment protection and benefit of executive soil resources in Taiwan. The revisions of related regulations and control standards will be more concerned about health risks, crop production, food safety, the status of soil background and also the properties of the contaminants, which may be hazardous in different pathways. In addition, the control standards (regulations) of other countries were also referred. In addition, zoning management according to land use types for land quality management, it has become a trend in many countries and different standards of a contaminant were made among the categories of land uses. The zoning management was also involved according to the economic and social development in Taiwan. An integrated assessment of the soil control standards of heavy metals was made and the new revisions have been suggested after risk-based approached values.

The present SPCSs in Taiwan and the suggested new revision were listed in Table 20 for comparison. Addition of the soil control standards of As, Cd, Cr(VI), Cu, Hg, Ni, and Pb in industry park area were recommended according to the lower risks, which accept higher metal levels in this area compared with present control standards for normal areas and rural lands. Compared to the present SPCSs, the suggested value of As and Pb which can pose high risks were revised to lower values for both rural land and normal land, while those of Cu and Zn were kept at the present value or higher value only for normal land. The SPCS of total Cr was strongly suggested to be replaced by those of Cr(III) and Cr(VI) for more efficient soil management of Cr pollutions. Table 21 shows the statistical results of worldwide regulatory guidance values of soil heavy metals which were applicable for the residential areas. The suggested revision of SPCSs in Taiwan is more close to the world trend of soil management of metals-contaminated soils.
Table 20. The suggested revision of Soil Pollution Control Standards (SPCSs) based on the integrated assessment and present regulatory values

<table>
<thead>
<tr>
<th>Metal element</th>
<th>Present regulations of SPCSs (mg/kg)</th>
<th>Suggested revisions of SPCSs (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rural land</td>
<td>Normal land</td>
</tr>
<tr>
<td>As</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Cd</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Cr</td>
<td>Total: 250</td>
<td>Total: 250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>200</td>
<td>400</td>
</tr>
<tr>
<td>Hg</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Ni</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Pb</td>
<td>500</td>
<td>2,000</td>
</tr>
<tr>
<td>Zn</td>
<td>600</td>
<td>2,000</td>
</tr>
</tbody>
</table>

¶: “—“ no recommended value; “?” need more communication.

Table 21. Comparison of the regulatory guidance values (mg/kg) of soil heavy metals applicable for residential areas in Taiwan and in other countries

<table>
<thead>
<tr>
<th>Element</th>
<th>Median (mg/kg)</th>
<th>Arithmetic mean (mg/kg)</th>
<th>Geometric mean (mg/kg)</th>
<th>Taiwan (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>USA</td>
<td>Other countries</td>
<td>USA</td>
<td>Other countries</td>
</tr>
<tr>
<td>As</td>
<td>20</td>
<td>135</td>
<td>44.3</td>
<td>0.61</td>
</tr>
<tr>
<td>Cd</td>
<td>7</td>
<td>1,408</td>
<td>11.2</td>
<td>26.5</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>250</td>
<td>74,000</td>
<td>19,100</td>
<td>8,100</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>100</td>
<td>398</td>
<td>921</td>
<td>46.4</td>
</tr>
<tr>
<td>Cu</td>
<td>200</td>
<td>2,860</td>
<td>1,550</td>
<td>1,030</td>
</tr>
<tr>
<td>Hg</td>
<td>3.5</td>
<td>28.7</td>
<td>16.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Ni</td>
<td>112</td>
<td>2,620</td>
<td>230</td>
<td>583</td>
</tr>
<tr>
<td>Pb</td>
<td>260</td>
<td>412</td>
<td>278</td>
<td>268</td>
</tr>
<tr>
<td>Zn</td>
<td>600</td>
<td>19,600</td>
<td>2,580</td>
<td>5,970</td>
</tr>
</tbody>
</table>

The values except for those of Taiwan were adapted from Jennings (2013).

Acknowledgement
The authors thank Taiwan Environmental Protection Administration (Taiwan EPA) to provide the financial supporting for this study project in 2013-2014. The authors also thank Taiwan Agricultural Research Institute (TARI) to provide several local field research databases collected from the heavy metals-contaminated sites in different regions of Taiwan.

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In-situ Immobilization of Selected Heavy Metals in Soils using Agricultural Wastes and Industrial By-products

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Abstract: Malaysian soils dominantly fall (about 75%) into the Ultisol and Oxisol Orders in Soil Taxonomy. These soils are generally acidic, pH of 4.0-5.0 and contain essentially of variable charge minerals, namely sesquioxides and kaolinite, thus, have low cation exchange capacity or cations retention capacity. Factors controlling heavy metals reactions and mobility in the soil system are pH, CEC, redox potential, etc. and these parameters will be exploited in the management of heavy metals contaminated soils. Amongst the remediation techniques opted are liming, in-situ chemical stabilization using agricultural wastes converted to biochars, such as oil palm empty fruit bunch and rice husk biochars, and industrial by-products such as red gypsum, coal fly ash and water treatment residue, to be applied as soil amendments.

Key words: Acidic soil, liming, biochar, red gypsum, coal fly ash, drinking-water treatment residue

1. Introduction

From our earlier work undertaken to study the heavy metals distribution in agricultural soils of Malaysia (Zarcinas et al., 2004), concentrations of Co, Ni, Pb and Zn in the soils were strongly correlated with soils concentrations of Al and Fe, which suggest evidence of background variations due to changes in soil mineralogy. Chromium was correlated with pH and EC, Na, S and Ca suggesting association with acid sulphate soil and soil salinity components, while Hg was not correlated with any of these components, suggesting diffuse pollution by aerial deposition. Arsenic, Cd, Cu were strongly associated with aqua-regia soluble and available P, and organic matter suggesting these metals are associated with agricultural inputs in agricultural fertilisers and soil organic amendments. This indicates heavy metal contamination to the majority of agricultural soils in Peninsular Malaysia is due to anthropogenic activity (possibly added in fertilizers, wastes, pesticides, effluents or atmospheric sources) that may pose a risk to the environment or human health.

The application of biochar to soil may also improve the sorption capacity of trace elements or heavy metals in soil. This carbonaceous product was reported to have many functional groups with high surface areas, which are likely related to its potential to act as an adsorbent. Heavy metal incorporation in the soil is controlled by adsorption processes, such as surface complexation and ionic exchange, but other mechanisms such as precipitation are likely to contribute to metal retention in the soil (Sastre et al., 2006). Adsorption is defined as the accumulation of ions at the interface between a solid phase and an aqueous phase. Adsorption isotherms have been widely used in studies on adsorption phenomena, supplying numerical parameters that provide information on the retention capacity and intensity of the metal by the soil (Casagrande et al., 2008). The advantage of these equations is that they can be applied to adsorption of any ions and gives straightforward parameters which can be related to soil properties. A number of studies have also demonstrated that biochar has a high capacity to adsorb pollutants in contaminated soils (Beesley et al. 2011; Yuan and Xu, 2011). Biochar can stabilize the heavy metals in the contaminated soils, improve the quality of the contaminated soil and has a significant reduction in crop uptake of heavy metals.

In many cases, a byproduct may not be ideal by itself for land application. Through co-utilization of byproducts, more products that are agronomically useful may result. The benefits of co-utilization may include nutrient balance, reduction of toxins or contaminants, improved moisture content, improved economic value, and improved soil conditioning effects. In-situ immobilization is a cost-effective approach where land-applied amendments are used to stabilize contaminants via adsorption and/or precipitation reactions that render the contaminant immobile (Adriano, 1986). Numerous inorganic amendments such as clays, Al/Fe/Mn oxides and hydroxides may be land applied to metal contaminated soils as means of reducing metal mobility. Nowadays, there is pressure on waste
management managers to find ways to convert wastes into resources instead of sending them to the landfill. Amongst the mineral wastes recommended for in-situ immobilization of heavy metals are red gypsum, coal fly ash and drinking water treatment residues. There has also been report that combination of mineral byproducts with biosolids or organic materials is in fact a more viable option than applying the byproducts singly for soil fertility improvement for crop production.

2. Liming

In Malaysia, liming is the most common management practice used to overcome the problems associated with soil acidification. Most plants grow well at a pH range of 5.5–6.5 and liming is aimed to maintain the pH at this range. The main purpose of liming is to reduce aluminium toxicity in highly weathered acidic tropical soil, but at the same time, this practice can help reduce heavy metals availability to plants via precipitation process. In a study on an Oxisol grown with cocoa, the application of lime at 2 t ha\(^{-1}\) reduced soil solution Mn concentration in the 0-15 cm layer from 27 to 12 µM after 3 months (Shamshuddin et al., 1991).

3. Biochar

In term of remediation of heavy metal contaminated soils through their retention in the soil system, biochar has been considered to be potentially effective. Biochar is a fine-grained charcoal-like material produced through pyrolysis, which is heating of biomass to temperature of 300-600 °C under air deprived conditions. Through pyrolysis, the feedstock changes chemically to form structures that are more resistant to microbial degradation than the original material.

Utilization of biochar as a soil amendment has attracted great interest globally due to the apparent benefits to soil fertility and plant growth as well as the potential to store or sequester C in the soil system. It has been reported that activated carbon, which is a subset of biochar, had been used as a substrate to improve the adsorption of heavy metals such as mercury, a process which is termed as chemisorption. The mechanism of heavy metal retention in soil by biochar can be categorized as physical or chemical in nature. The physical aspects deal more with filtering mechanism of the heavy metal due to its structure or size by the pore size of the biochar. It is important to characterize the pore size distribution of biochar, the percentage of macropore, mesopore, nanopore, because the type of pores dictate the extent of liquid-solid adsorption processes.

In Malaysia, a pilot scale biochar manufacturing plant using a modern engineering system has been built by Universiti Putra Malaysia (UPM), in collaboration with a private company (Nasmech Technology Sdn. Bhd.). The plant was built to produce biochar from oil palm empty fruit bunches (EFB) and is capable of producing 20 t of biochar daily. Additionally, biochar derived from rice husks has been produced commercially in Malaysia to avert wastage of large quantities of rice husks (RH). It is reported that 97,980 million tonnes of rice husk was produced annually during the processing in the mills (Bernas Sdn. Bhd.).

The surface morphology of biochar samples was observed under Jeol JSM-6400 scanning electron microscope. Figure 1 shows that EFB biochar possesses uniform pores and smooth wall surfaces with maximal 20 µm in diameter. Small particle-like ashes were found scattered on the surface area of EFB biochar as observed in Figure 1a. In comparison, the pores on rice husk biochar are not well-shaped with diminished structure of pores (Figure 1b). Small pores on the rough rice husk biochar surface was observed as shown in Figure 2. Pyrolysis temperature can attribute to the pores formation and destruction on biochar. When low temperature was applied, the biochar cell structure and arrangement was found similar to the cell structure and arrangement of the original biomass (Pavithra, 2011). The stack of biochar cells and pores were arranged accordingly and well-shaped as found in the SEM image of EFB biochar. However, as the temperature increase, the pore size become enlarged and the walls between adjacent pores were destroyed (Zhang et al., 2004), which explained the diminish pores
on rice husk biochar. The lack of biochar structure also might be due to the volatilization process during the biochar production.

From the observation on the SEM images, both biochar generally exhibit macropores with internal diameter size of 10 μm. The macroporosity (>50 nm) of biochars are relevant for soil aeration and water movement (Troeh and Thompson, 2005). Macropores also facilitate the root movement through the soil and act as habitats for the soil microbes (Saito and Muramoto, 2002). Hence, biochar has the potential to improve soil physical properties such as soil water retention and porosity. Basso et al., (2013) reported the addition of biochar on sandy loam soil increased the water-holding capacity by 23% compared to the non-amended soil. Glaser et al. (2002) also found the increase of soil field capacity with the increase of char surface area and porous structure. The macropores are also important as feeder pores to transport adsorbate molecules to the meso- and micropores.

A mixture of meso- and micropores were also present on EFB and rice husk biochar surface. The micropores of biochar make the greatest contribution to total surface area, hence responsible for the high adsorption capacities of molecules (Rouquerol et al., 1999). Mesopores are also of importance for many liquid-solid adsorption processes, as reported by Lua et al., (2004), on pistachio-nut shells. Thus, based on the EFB and rice husk biochar structural surface, they have the potential to sorb metal and metalloid to reduce the mobility of these trace elements in soil.

![Figure 1. SEM image of EFB biochar at 1000 x magnification](image1)

![Figure 2. SEM image of rice husk biochar at (a)1500 and (b)1000 x magnification](image2)
The Brunauer, Emmett and teller (BET) surface area of biochar indicates the physical changes of biomass during the pyrolysis process. The surface area depends largely upon the carbon (C) mass removed during the processing, creating pores in the materials (Zabaniotou et al., 2008). The sorption ability of biochar can be determined from its surface area, where high surface area will increase the sorption capacity. Surface area and porosity of EFB and rice husk biochar are presented in Table 1.

Table 1: BET surface area and porosity of biochars

<table>
<thead>
<tr>
<th>Biochar</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore surface area (m²/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFB</td>
<td>46.32</td>
<td>0.01</td>
<td>0.61</td>
<td>3.85</td>
</tr>
<tr>
<td>Rice husk</td>
<td>23.22</td>
<td>0.01</td>
<td>1.41</td>
<td>4.34</td>
</tr>
</tbody>
</table>

Biochar produced from EFB had a larger surface area than RH biochar. The higher surfaces area of EFB biochar may indicate the adsorption capacity of heavy metals compared to RH biochar. In general, biochar surface areas can be influenced by biochar’s micropore volume, choice of feedstock and pyrolysis processing condition (Boateng et al., 2007). The micropore volume of EFB biochar was found to be same as RH biochar (~0.01 cm³/g). Internal surface area of biochar which represent pore on the inner wall resulted from interior crack was referred to as micropore area. Meanwhile, the average pore diameter for both biochar are in the range of mesopores diameters, with the internal pore width between 2 to 50 nm. This indicates the potential of adsorption capacity EFB biochar and RH biochar in liquid-solid adsorption (Bagreev et al., 2001).

The adsorption isotherm data were fitted to the Langmuir’s adsorption model. Table 2 shows the values of adsorption isotherm parameters for EFB biochar and RH biochar. The maximum adsorption capacity (qₘₐₓ) of EFB biochar for As was 0.424 mg g⁻¹, which is higher than RH biochar (0.352 mg g⁻¹). Similar trend was found on qₘₐₓ of Cd with the values of 15.15 and 3.19 mg g⁻¹, for EFB biochar and RH biochar, respectively. The parameter b is related to the affinity of the binding sites, which allows comparisons of the affinity of biochar toward the metalloid ions. EFB biochar had a higher affinity for As than did RH biochar. In contrast, the binding affinity (b) of Cd for RH biochar is higher than EFB biochar. There are several factors attributed to sorption mechanism of trace elements with addition of biochar, of which the most important are pH and CEC (Kumpiene et al., 2008). The alkaline properties of biochars increased the solution pH, which induced metal immobilization through metal precipitation and decreases metal solubility (Rees et al., 2013). Value of R² shows correlation or linear relationship, whereas the relationship become more linear when the value is closer to 1. The high correlation coefficient values (R²) which ranged from 0.98 to 0.99 indicate that the Langmuir isotherm best fitted the experimental data.

Table 2: Sorption isotherm obtained by fitting the data with the Langmuir isotherms for the EFB biochar and RH biochar

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Heavy metal</th>
<th>qₘₐₓ (mg g⁻¹)</th>
<th>b (L mg⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFB</td>
<td>As</td>
<td>0.4240</td>
<td>0.7299</td>
<td>0.9890</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>15.1515</td>
<td>0.1142</td>
<td>0.9921</td>
</tr>
<tr>
<td>RH</td>
<td>As</td>
<td>0.3522</td>
<td>0.0248</td>
<td>0.9823</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>3.1908</td>
<td>0.6920</td>
<td>0.9984</td>
</tr>
</tbody>
</table>
Samsuri et al. (2013) reported coating the biochars with Fe (III) greatly increased their adsorption capacities for both As (III) and As (V). The results indicate that the commercially produced EFB and RH from Malaysia have good potentials to be used as adsorbents for As (III) from aqueous solutions. Furthermore, coating the EFB and RH with Fe (III) increased their adsorption capacities for both As (III) and As (V) making the biochars more effective as adsorbents for both As (III) and As (V).

Soil solution study of incubated arsenic-rich Histosol amended with biochar was conducted to evaluate the effects of EFB biochar and RH biochar on water-soluble As naturally present in Histosol (Figure 3). Empty fruit bunch and RH biochars exhibit important feature as adsorbent with the porous structure and alkaline properties. The sorption experiment has shown the potential of these biochars to immobilize As in the soil system. The decreased of As concentration and increased of soil pH in soil solution study indicate the ability of biochar to reduce the phytoavailable As in contaminated soil (Figure 4).

![Figure 3: Effects of biochar on water-soluble arsenic in pore water](image)

![Figure 4: Effects of biochar on extractable arsenic in soil](image)
The pot experiment was conducted to determine the optimum rates of biochars to reduce arsenic (As) uptake by sweet corn (Figure 5). Two types of biochars, EFB and RH with 5 rates (0, 2.5, 5, 10, 20 t C/ha) application were applied to 15 kg naturally contaminated soil in polybag. After 56 days of growth, biochar reduced the concentration of As in foliar tissue by 58% and 61% with the highest application of EFB and RH biochars at 20 t/ha C compared to the non-amended soil. The study shows the effectiveness of biochar in reducing the availability of As uptake by sweet corn as trace elements concentration decreased with increasing rate of biochar.

Figure 5. The uptake of arsenic by sweet corn plant after 56 days of planting

4. Industrial by-Products

Addition of industrial by-products to soil has gained importance recently as an alternative to remediate heavy metal contaminated soil. For example, byproducts from steel (iron oxides) and energy industries (ashes) will be assessed as an environmentally and resource-efficient option due to their alkalinity or acid neutralizing capacity and high specific surface area. The ANC is usually expressed as CaCO₃ equivalent and one of the most important factors used to evaluate the value of industrial byproducts to be used as a liming agent on acidic soil.

4.1 Red Gypsum

Red gypsum (RG) is a waste material from the extraction of Ti for industrial purposes. Titanium is extracted from the mineral ilmenite (FeTiO₃) by sulfuric acid digestion. Red gypsum is produced by further increasing the pH of the effluent to about 5.0 by using calcitic limestone (CaCO₃), at which point the remaining sulfate precipitates along with iron oxides. The latter, derived from the iron contents of the ilmenite, are responsible for the red color of the material. Normally, this waste product is disposed off outside the titanium dioxide plant. Such byproducts might be suitable for use in agriculture in situations where mined gypsum has been used in the past. Red gypsum can be of great economic value due to its very high Ca and S content. Moreover, there are several reports on application of red gypsum as a soil amendment to immobilize As, Cd, Cu and Pb in heavy metal-contaminated soils (Lombi et al., 2004; Illera et al., 2004). In addition, the presence of the iron oxide responsible for the red color of RG might make it more effective as a soil amendment (Fauziah et al., 1996) rather than as a source of Ca and S fertilizer. Dissolution of the gypsum and subsequent supply of sulfate S to crops might be affected by the presence of the oxides, which have the possibility to adsorb sulfate.
The RG was alkaline in nature, with a pH of 7.98 due to the presence of residual CaCO$_3$ in RG (Fauziah et al., 1996). This property can be exploited to reduce the solubility and hence, phyto-availability, of some heavy metals in the soil system. The acid neutralizing capacity is the most important characteristic in evaluation of the value of the material as a liming agent. Red gypsum is not a good liming agent, with only 1.79% calcium carbonate equivalence. However, high rates of application (> 2.5%) can have significant influence on the pH of the soil system (Nur Hanani et al., 2009). Iron oxide-rich gypsum by-products, including red gypsum (119 m$^2$ g$^{-1}$), have very large surface areas (Peacock and David, 2000). The surface area for the red gypsum (pulverized and sieved through 2.0 mm sieve size) was 39.8 m$^2$ g$^{-1}$. The high surface area plays a central role for adsorption behavior. Furthermore, the presence of Fe oxide can contribute to the co-existence of positive and negative charges on the variable charge oxide surface (Figure 6).

A column leaching study was conducted to investigate the red gypsum for in-situ immobilization of arsenic in the soil system. In this experiment, the treatment used was the different rates of red gypsum. The treatments were applied at the top soil only. The treatments were: T1 : no red gypsum (control), T2 : 25 t/ha red gypsum, T3 : 50 t/ha red gypsum, T4 : 100 t/ha red gypsum. From this study, red gypsum application has the potential to immobilize arsenic in the soil system and thus prevent arsenic from being taken up by the crop grown on arsenic contaminated soil. The presence of Fe in red gypsum can help surface adsorbed or co-precipitate As in the soil system (Figure 7 and 8).

![Figure 6: Fibrous Crystal Aggregates of Gypsum with Some Coatings of Iron Oxides](image)

![Figure 7: Arsenic concentration in each of the leachate collection (50 ml) up to one pore volume for each treatment.](image)
In a soil incubation study, RG was applied to sewage sludge treated soil. Sewage sludge tend to have high concentrations of Cu and Zn and its application to soil increase these metals content. There seemed to be a lag-phase in the release of Zn from the RG minerals into the soil solution (Figure 9). The Zn concentrations in the soil solution started to increase only after 5 weeks of incubation for the treatments with low rates of RG application. The reason for this slow release of Zn into the soil solution is not known. However, this study demonstrated that increasing the RG amendment rates (5%, 10%, 20% and 40%) clearly reduced the Zn concentrations in soil solution after ten weeks of incubation. Thus, RG has the potential to fix Zn in the soil system and make it less phyto-available.

Increasing the rate of red gypsum application resulted in decreasing uptake of Zn, Cu and Fe by the corn plants (Figure 10). This is due to the increase in soil pH. The residual alkalinity plus the buffer capacity of iron oxides (goethite and hematite) (Fauziah et al., 1996), allow red gypsum to consume protons from an acid soil. However, the results for Cr seemed to be rather varied. The grasses grown on heavy metals contaminated soil remediated with red mud (a by-product of the bauxite industry) had high Cr concentrations (Zhao et al., 2005; Snars et al., 2004). Thus, there may be room for speculation that RG also contain high levels of Cr. However, the levels of Cr in red gypsum were found to be low.
This study did not ascertain whether the organic matter in sludge alleviates the effect of excess Ca and Fe in the mixed soil system. This needs to be investigated. Furthermore, co-mixing two products such as RG and compost can turn the by-products into a more useful soil amendment as the amending capability of the by-product can be complemented and further enhanced by the co-mixed by-products (Fauziah et al., 2011).

![Graphs showing uptake of Zn, Cu, Fe, and Cr](image)

Similar letters above bars indicate that the values represented by the bars are not significantly different at the 1% level, according to the Duncan New Multiple Range Test (DMRT)

Figure 10: Uptake of microelements (mg/pot) using contaminated soil amended with red gypsum

A glasshouse study was then conducted with the same treatments as the soil incubation study using sweet corn as the test crop. Two set of experiments were established with 4 treatments and 4 replicates. Treatments of experiment are: Red Gypsum + EFB Compost with different rate of red gypsum (2.5, 50, 100 and 200 t/ha) (Table 3). For Fe concentrations, application of RG+EFB compost show significant decrease in Fe concentrations in foliar tissues at the rate of 100 and 200 t/ha compared to the lower rates. The toxic level of Fe for corn is >350 mg/kg, thus there is no problem of Fe toxicity to plants in this case. For Zn concentration, significant decrease in Zn concentration were found at the rates of 100 and 200 t/ha compared to the lowest rate of RG. For Cd, significant decreased in Cd concentrations with the increasing rates of RG+EFB compost found at the rates of 100 t/ha and 200 t/ha compared to the lowest rate of RG+EFB compost used.
Table 3: Effects of treatments on heavy metals in foliar tissues

<table>
<thead>
<tr>
<th>Treatment</th>
<th>mg/kg</th>
<th>Fe</th>
<th>Zn</th>
<th>Cd</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>RG 2.5t/ha + EFB Compost</td>
<td>305 ab</td>
<td>83.75 a</td>
<td>0.16 ab</td>
<td>0.98 ab</td>
<td></td>
</tr>
<tr>
<td>RG 50t/ha + EFB Compost</td>
<td>477 ab</td>
<td>75.65 a</td>
<td>0.08 ab</td>
<td>0.07 b</td>
<td></td>
</tr>
<tr>
<td>RG 100t/ha + EFB Compost</td>
<td>237 bc</td>
<td>39.20 b</td>
<td>0.03 b</td>
<td>0.14 ab</td>
<td></td>
</tr>
<tr>
<td>RG 200t/ha + EFB Compost</td>
<td>94 bc</td>
<td>9.63 b</td>
<td>0.05 b</td>
<td>0.06 b</td>
<td></td>
</tr>
</tbody>
</table>

Mean having the same letters within column are not significantly different at p>0.05

4.2 Coal Fly Ash

Coal fly ash (CFA) is an amorphous aluminosilicate material, a by-product of coal combustion and is composed of particulate matter collected from flue gas stream. Coal is one of the alternative natural resources used for the production of electricity in Malaysia. The increase use of coal for electric power generation will generate large quantities of CFA. Kapar power station in Selangor, Malaysia, produced around 200 Mg CFA per day. Currently, only 20% of the CFA is utilized as a component in the cement mixture, the rest is left stacked within the vicinity of the power plant.

Coal is known to contain every naturally occurring element, and therefore, it is not surprising that CFA can have beneficial effect on solving certain problem of soil quality. Use of CFA as a soil amendment is hindered by the lack of macronutrients in the ash and also concern its high concentration of microelements, especially boron. The CFA is an alkaline residue produced during the burning coal for the generation of electricity which is enriched with CaO and MgO and has a pH around 8 to 12. The pH of CFA can vary depending on the S contents of the coal source, with high S generally producing acidic material and low S producing alkaline material (Adriano et al., 2002). The pH of CFA used in this study was 8.34. In some cases, alkaline agent was used as a stabilization agent for contaminated soil to reduce pathogen and heavy metals availability (McGrath et al., 1995; Zhang et al., 2007).

Large surface area determination of CFA was probably due to large number of spongy irregular carbon-rich particles of unburnt coal (Fauziah, 1993). Surface area determination for this CFA was 7.5 m²/g. Hence, the particle size distribution will provide information relating to land application of the ash, in term of trace elements solubility and effect on soil physical properties (Figure 11).

Figure 11: Cenophere Shape of Coal Fly Ash
The neutralization of acid by CFA is a relatively slow process that mainly involves the particle surfaces (Wong et al., 2002). The CFA was not a good liming agent, with only 0.504% CaCO$_3$ equivalent (CCE). Based on the low level of Ca this CFA, it is considered only as a Class F fly ash (Bilski et al., 1995). Therefore, considerably large quantities of this CFA compared to lime will be required to raise the pH of soil to some target level.

A soil incubation study was also conducted whereby, CFA was applied on sewage sludge treated soil. Increasing the CFA amendment rates clearly reduced the Zn concentrations in soil solution for the ten weeks of incubation (Figure 12). The reduced concentration of Zn probably can be explained by the higher adsorption and precipitation of Zn with an increase in pH (Sims and Kline, 1991; Jackson et al., 1999). The control treatment (0% CFA) had Zn concentrations in the soil solution ranged from 1.47 mg L$^{-1}$ to 0.67 mg L$^{-1}$ for the four weeks of incubation and increased drastically at week five to 5.0 mg L$^{-1}$. It is not known with certainty why there was a delayed dissolution of Zn from the sewage sludge. The Zn concentration for the control treatment after week five until week ten of the incubation was still high (> 3.73 mg L$^{-1}$) compared to other treatments. Treatments using 2.5% and 5% CFA ranged less than 2.15 mg L$^{-1}$ whereas treatments using greater than 10% CFA had the lowest Zn concentrations which were less than 1 mg L$^{-1}$. This indicates that CFA was feasible as a stabilization agent to reduce heavy metal toxicity in the sewage sludge-treated soil.

![Figure 12: Soluble Zn at different rates of CFA-contaminated soil treatments](image)

The Zn uptake by maize for treatment using CFA is shown in Figure. Overall, the concentration of Zn uptake by maize significantly decreased at higher rates of CFA treatments. Usage of 2.5% CFA did not show any significant result as compared to the control treatment. However, addition of more than 5% CFA significantly reduced Zn concentration in maize. This showed that the CFA was useful as a soil amendment to fix Zn in the contaminated soil.

The results showed application of CFA up to 10% reduced Cu uptake by the maize plants compared to the control (Figure 13). However, there was no significant difference in Cu uptake by maize between the control and the 20% CFA treatment indicating that CFA can be beneficial as a soil amendment to reduce Cu uptake by plant but, the amount of CFA should be applied at a proper rate to avoid Cu toxicity (Nur Hanani et al., 2010).
4.3 Drinking-water Treatment Residues (WTRs)

In Malaysia, a low-cost and potentially effective substitute for remediation could be drinking-water treatment residues (WTRs). The pH for WTR for this study was close to being neutral just as stated in the reports of Gallimore et al., (1999), Ippolito et al., (2000) and Elliot et al., (1990). The WTR has a pH of 7.07, the mineral present in WTR, such as kaolinite, gibbsite and Fe-oxides, provide surfaces for the adsorption of heavy metals. Value for WTR surface area was 28.3 m²/g and this value was largely dependent on the size of the sample which was less than 2 mm due to the grinding process. Surface area determination can be used to estimate the amount of surface sites available for surface complexation reaction (Figure 14). Butkus (1998) reported a surface area of WTR was 10 m²/g. Dzombak and Morel (1990) estimated that WTR can bind with protons, cations and anions based on the range of sorption maxima reported from 160 m²/g to 600 m²/g. The ANC of WTR was 0.504% CCE. Thus, WTR cannot be considered a good liming material compared to the pure CaCO₃, but perhaps usage at high rates of this material can still increase the pH of acidic soil.

Also, in an incubation study of sewage sludge treated soil, treatment using the highest rates of WTR (40%) gave the lowest Zn concentration in the soil solution (Figure 15). Perhaps, the high Zn concentrations and high pHs at the higher WTR rates led to low solubility of Zn due to the pH effect and also the phenomenon call ageing (Lock and Janssen, 2003). The trend of Zn solubility indicates slow dissolution of Zn minerals at the initial stage, and then the concentration dropped again due to the precipitation or ageing affect. Zinc concentrations were found to be low in all treatments using different rates of WTR (2.5, 5, 10, 20, and 40%) compared to the control (0% WTR). Addition of WTR did reduce the release of Zn from the sewage sludge. Therefore, WTR can be considered to be a potential soil amendment to fix Zn in contaminated soils.
Figure 14: Presence of Kaolinite (Hexagonal Shape) and Illite Flakes of WTR

Figure 15: Soluble Zn at different rates of WTR-contaminated soil treatments

Addition of WTR significantly reduced Zn uptake by corn plants compared to the control (Figure 16). This results show that the usage of WTR mixed with sewage sludge can significantly reduce the Zn uptake by corn. The major effect of high pH was to reduce the solubility of all micronutrients, especially Zn. Meanwhile, addition of more than 5% WTR, significantly reduced Cu uptake compared to the control. This results show that the usage of more than 5% WTR in sewage-sludge-amended soil can significantly reduce the Cu uptake by corn (Nur Hanani et al., 2008).
Similar letters above bars indicate that the values represented by the bars are not significantly different at the 1% level, according to the Duncan New Multiple Range Test (DMRT).

Figure 16. Uptake of heavy metals, Zn and Cu (mg/pot) using soil amended with WTR

5. Conclusion

There is great potential of biochar and industrial byproducts utilization in agricultural soils in term of heavy metals immobilization. More work should be conducted on producing high quality biochar. For biochar, a community scale carbonator of low cost need to be developed. For the industrial byproducts, they should be easily accessible for farmers’ utilization.

6. Acknowledgement

We would like to thank UPM for giving us the permission to carry out this project under the Fundamental Research Grant Scheme and also to publish this research work.

7. References


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Level of Heavy Metals in Agricultural Soil and Water after Mount Sinabung Eruption in North Sumatera, Indonesia

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Abstract: Mount Sinabung on the Indonesian island of Sumatra is a 2,460-metre-high volcano which has been spewing molten lava and suffocating ash since September last year. Mount Sinabung has erupted more than 200 times since 2010. Sand material mixed with dust cover agricultural area covering a radius of 2.5 kilometers, especially to the west. The volcanic ash is also considered to have an impact on the quality of agricultural products consumed by humans and agricultural environment (soil and water). This study conducted in Dec 2013 and Feb 2014 were aimed to determine the levels of heavy metals in agricultural soil, and water around Mount Sinabung which covered volcanic ash. The samples were collected from several location (1,200-1,300 metres above sea level) such as at Mardinding, Sukanalu, Kutarayat, Kutagugung, Kutatunggal villages. Concentration of heavy metals, namely Cd, As, Cu, Pb, Mn, Fe, Mg, and Zn were determined by atomic absorption spectrometry. Levels of heavy metals were compared with the permitted values by Indonesian government regulations. Results indicated that the concentration of heavy metals in volcanic ash were Mg 6.6, Mn 321.0, Fe 58.2, and Pb 126.3 µg/g. Concentration of heavy metals in river water were As < 0.001, Cd < 0.02, Cu < 0.02, Pb < 0.03, and Zn < 0.02 – 0.046 mg/L. Concentration of heavy metals in water of the lake Mardingding were Mn 0.14, and Zn 0.02 mg/L. Concentration of heavy metals in soil were Cu 0.61-1.17, Pb 0.10-0.23, and Zn 20.5-37.9 µg/g. The concentration of Zn in river water have exceeded the standard concentration for fisheries and livestock water (Indonesian Government Regulations No. 20, 1990) of 0.02 mg/L. The presence of heavy metals in soil and water indicates the potential for pollution transfer from these media to food chain.

Key Words: Heavy metal, Mount Sinabung eruption, North Sumatera

Introduction

Indonesia is known as a country that has the highest active volcano in the world (more than 30% of the active volcanoes in Indonesia). Mount Sinabung is one of about 130 active volcanoes in Indonesia. Mount Sinabung is a Pleistocene-to-Holocene stratovolcano of andesite and dacite in the Karo plateau of Karo District, North Sumatra, Indonesia, 25 miles from Lake Toba supervolcano. The volcano had been inactive for over four centuries, with the most recent eruption occurring in 1600. Solfatara activities (cracks where steam, gas, and lava are emitted) were last observed at the summit in 1912; recent documented events include an eruption in the early hours of 29 August 2010 and eruptions in September and November 2013, January and February 2014. Mount Sinabung has erupted many times. Since the eruption, Mount Sinabung has been very active in terms of having explosions of ash up to 2 times a day. There are more than 200 eruptions recorded since August 2013 with the last was in June 2014.

The eruption of Mount Sinabung released hot clouds and volcanic ash. Volcanic ash to covered not only the streets and houses but also agricultural plants. Volcanic ash is the material most widely spread, and damage to crops, especially horticulture radius of 5 kilometers from the center of eruption. Volcanic ash impact on most of the villages and the villages that are in the 6 (six) districts around Mount Sinabung were District of Namanteran, District of Simpang Empat, District of Merdeka, District of Dolat Rayat, District of Barusjahe, and District of Berastagi.

The heavy metals have potent cumulative properties and toxicity due to which they have a potential hazardous effect not only on crop plants but also on human health. The metal contaminants can be reduced
by immobilization of contaminants using macrophytes and also by using genetically engineered microorganisms (Chopra et al., 2009). The presence of heavy metals in soil and water indicates the potential for pollution transfer from these media to the food chain (Alloway, 2004; Mwegoha and Kihampa, 2010). The heavy metals have a marked effect on the aquatic flora and fauna which through bio magnification enter the food chain and ultimately affect the human being as well (Sonawane et al., 2013).

Input of lead to agricultural soil occurs through atmospheric deposition of lead derived from combustion of gasoline containing lead additives and from fugitive emissions from nonferrous metal smelting (Alloway, 1990). Total metal content of soil is useful for geochemical purposes but their speciation (bioavailability) is of more interest agriculturally and this entails the identification and quantification of the different, defined phases in which the metals occur which can help assess how strongly they are retained in the soil. (Zimmerman and Weindorf, 2010)

The correlation of both high heavy metal (Hg) domains in the Lake Moreno Oeste and Lake Ton’cek sequences with records of extended fires in the region suggests that this source, as well as the volcanic activity, could have generated the high levels and variations of Hg concentrations and accumulation rates observed in these pristine lakes already in pre-industrial times (Guevara et al., 2010).

Many researchers have shown that volcanic ash contains heavy metals elements. From the interactions between volcanic ash and human, the danger from volcanic ash containing heavy metals can be categorized into two: breathing and environmental risks. Breathing volcanic ash may lead to the risk of cancer due to radionuclide deposit in the respiratory system. Heavy metals in the environment will expose the humans in the vicinity.

Stewart et al (2006) reported that devised a simple model using volcanic ash leachate composition data to predict effects on receiving waters. Applying this model to the effects of Ruapehu ash, from the 1995/1996 eruptions, suggests that the primary effects of concern are likely to be an increase in acidity (decrease in pH), and increases in concentrations of the metals aluminium, iron and manganese. These metals are not normally considered to pose health risks, and are regulated only by secondary, non-enforceable guidelines. However, exceedences of guideline values for Al, Mn, Fe and pH will cause water to become undrinkable due to a bitter metallic taste and dark colour, and may also cause corrosion, staining and scale deposition problems in water tanks and pipes. Therefore, the main issues following volcanic ashfall of similar composition to Ruapehu ash are likely to be shortages of potable water and damage to distribution systems, rather than risks to public health.

The weathering indices can be used to quantify the condition of the volcanic ashes at the initial stage of weathering, to evaluate their fertility, to provide a better understanding of element mobility during weathering, and predict the source of soil nutrients as well as determine the products of primary minerals alteration (Fiantis et al., 2010).

Gabrielli et al (2008) reported that A well-defined peak of Pt, and a spike of Ir, were found at the base of the snow pit record. These maxima occur in close concurrence with large concentration peaks in Cd.

Zincite probably results from the reaction between steam, air and magmatic zinc halide. Thermodynamic calculations indicate that oxidation of zinc halide proceeds under the prevailing conditions in the eruption cloud. The zinc enrichment in the phreatic ashes adds evidence to the hypothesis that magmatic vapors were involved in the phreatic eruptions. It appears as if zinc is released from the magma already in the earliest stages of volcanism; monitoring of zinc in fumaroles and hot springs could possibly be helpful in the prediction of volcanic activity (Thomas et al., 1982).

This paper presents the results of the heavy metals survey carried out in several village close to Mount Sinabung crater during the recent eruption. We focus on the abundance of the heavy metals namely Cd, As, Cu, Pb, Mn, Fe, Mg, and Zn. Evaluation and interpretation of the distribution of these elements were searched and compared with the standard concentration for fisheries and livestock water (Indonesian Government Regulations No. 20, 1990)
Materials and Methods

Description of the study area

The study area is located at the vicinity of Mount Sinabung (coordinates 3° 10’ 12” N; 98° 23’ 31” E) in North Sumatera Province (Figure 1). The environmental measurements were conducted in situ at eight locations in the villages of Sukanalu, Kuta Rayat, Kuta Gugung, Sigarang-garang, Suka Tepu, Gamber, Kuta Tunggal and Mardinding, District of Karo, North Sumatera Province. They are situated about 3 km north-eastern of the volcano’s crater (the yellow nails on Fig. 1). The exact geographical position of the sampling locations is given in Table I. The measurements were carried out on 8-11 December 2013 and 19-22 February 2014. At the time of data acquisition the alert level of erupted volcano was level 3 (watch) (on a scale of 1-4).

Fig. 1 Map showed the location of Mount Sinabung in North Sumatera Province of Indonesia

Sampling

A total of 32 water and soil samples were collected from eight (8) sampling location between December 8-11, 2013 and February 19-22, 2014. The exact geographical position of the sampling location is given in Table 1.
Table 1. Geographical position of the sampling locations

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling Locations (Villages)</th>
<th>GPS Coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sukatepu</td>
<td>03.10.490 098.26.894</td>
</tr>
<tr>
<td>2.</td>
<td>Sukanalu</td>
<td>03.11.121 098.25.645</td>
</tr>
<tr>
<td>3.</td>
<td>Sigarang-garang</td>
<td>03.11.249 098.24.368</td>
</tr>
<tr>
<td>4.</td>
<td>Kuta Gugung</td>
<td>03.11.922 098.24.213</td>
</tr>
<tr>
<td>5.</td>
<td>Kuta Rayat</td>
<td>03.12.143 098.24.279</td>
</tr>
<tr>
<td>6.</td>
<td>Kuta Tunggal</td>
<td>03.09.429 098.25.473</td>
</tr>
<tr>
<td>7.</td>
<td>Gamber</td>
<td>03.09.245 098.25.643</td>
</tr>
<tr>
<td>8.</td>
<td>Mardinding</td>
<td>03.09.348 098.21.720</td>
</tr>
<tr>
<td>9.</td>
<td>Sukameriah</td>
<td>03.08.220 098.24.151</td>
</tr>
<tr>
<td>10.</td>
<td>Batu Karang</td>
<td>03.06.521 098.21.116</td>
</tr>
</tbody>
</table>

Fig. 2. Map of Distribution of Volcanic Material and sampling locations (red circles)

Collection of water samples

Water samples were collected using 500 mL plastic bottles. The sampling bottles for heavy metal determination were pre-soaked overnight with 10% HCl and rinsed with distilled water and rinsed using water sample before sample collection. Preservation of water samples was done by adding 2 drops of concentrated HNO₃ to each water sample before storage below 4°C until analyzed.

Collection of soil samples

Soil samples were collected at depth of 0 to 20 cm from locations, stored in plastic bags and transported to the laboratory for heavy metal extraction and analysis.
Soil sample preparation for heavy metal analysis

Selected physical and chemical soil properties were analyzed according to the Indonesian Soil Research Institute Method (ISRI, 2005). Soil samples were collected from cultivated field of Mt Sinabung agriculture area in the summer. The soil samples were oven dried at 105°C for 24 h, followed by grinding and sieving using 0.18 mm sieve. 0.5 g of dry soil sample was poured into a graduated test tube and mixed with 2 ml of aqua regia 1:3 (1 conc. HCl: 3 conc. HNO₃). The mixture was digested on a hot plate at 95°C for 1 h and allowed to cool to room temperature. The sample was then diluted to 10 ml using distilled water and left to settle overnight. The supernatant was filtered prior to analysis using AAS as specified in APHA (2005). The properties of soil, volcanic ash and cold lava are shown in Table 2.

Table 2. Soil, volcanic ash and cold lava properties

<table>
<thead>
<tr>
<th>Soil and volcanic ash and cold lava collected from</th>
<th>Texture and type</th>
<th>Clay content (%)</th>
<th>Carbon content (%)</th>
<th>CEC (m/z/100 g)</th>
<th>pH (H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuta Rayat (Soil)</td>
<td>Clay loam</td>
<td>22.5</td>
<td>6.43</td>
<td>20.02</td>
<td>5.6</td>
</tr>
<tr>
<td>Kuta Rayat</td>
<td>Clay loam, volcanic ash</td>
<td>13.0</td>
<td>0.54</td>
<td>6.13</td>
<td>4.5</td>
</tr>
<tr>
<td>Sukameriah</td>
<td>Clay loam, cold lava</td>
<td>18.0</td>
<td>0.71</td>
<td>7.99</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Analytical methods

Heavy metals

Analysis of heavy metals in soil and water samples was done using Varian AA240FS Atomic Absorption Spectrophotometer equipped with Varian VGA77 vapor generator and Varian SPS3 Autosampler with a computer interface for operation and readings display, Varian Spectra AAS with SpectraAA55.

Result and Discussion

Material of Mount Sinabung eruption that covers the agricultural area consist of sand, dust and lava flow. Volcanic ash of Mt. Sinabung are andesitic-dasitik, many containing silicates, so it can be cement when dry.

The summary of the concentration of heavy metals in the water and soil samples are listed in Table 4 and 5 respectively. Heavy metals such as As, Cd, Pb, Zn, Mn, Se, Cu and Fe were found almost in all locations. Generally the heavy metals levels in water samples were low. Concentration of Cd (in Sukatpeu, Sukanalu, Sigarang-garang, Kuta Gugung, Kuta Rayat, Kuta Tunggal, Gamber and Mardinding villages) and Zn (in Mardinding and Batu Karang villages) were higher than Indonesian Government Regulation (IGR) for Fisheries and Livestock. The content of heavy metals in water caused by the influence of loaded with pollutants from volcanic ash, which are known to contain heavy metals such as Pb, Mn and Fe (Table 3).
Table 3. Heavy metals concentration in volcanic ash

<table>
<thead>
<tr>
<th>Materials</th>
<th>As (mg/Kg)</th>
<th>Cd (mg/Kg)</th>
<th>Pb (mg/Kg)</th>
<th>Zn (mg/Kg)</th>
<th>Mn (mg/Kg)</th>
<th>Se (mg/Kg)</th>
<th>Cu (mg/Kg)</th>
<th>Fe (mg/Kg)</th>
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</thead>
<tbody>
<tr>
<td>Volcanic Ash</td>
<td>na</td>
<td>nd</td>
<td>16.58</td>
<td>na</td>
<td>28.22</td>
<td>na</td>
<td>na</td>
<td>80.75</td>
</tr>
</tbody>
</table>

Nd: not detection; na: no analysis

Table 4. Heavy metals concentration in water samples

<table>
<thead>
<tr>
<th>Sampling locations (villages, river/lake)</th>
<th>As (mg/L)</th>
<th>Cd (mg/L)</th>
<th>Pb (mg/L)</th>
<th>Zn (mg/L)</th>
<th>Mn (mg/L)</th>
<th>Se (mg/L)</th>
<th>Cu (mg/L)</th>
<th>Fe (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sukatepu</td>
<td>0.0004</td>
<td>0.0121</td>
<td>0.0214</td>
<td>0.0012</td>
<td>0.1011</td>
<td>0.0003</td>
<td>0.0122</td>
<td>0.0122</td>
</tr>
<tr>
<td>Sukanalu</td>
<td>0.0008</td>
<td>0.0182</td>
<td>0.0272</td>
<td>0.0460</td>
<td>0.1254</td>
<td>0.0006</td>
<td>0.0185</td>
<td>0.0140</td>
</tr>
<tr>
<td>Sigarang-garang</td>
<td>0.0006</td>
<td>0.0163</td>
<td>0.0241</td>
<td>0.0014</td>
<td>0.1122</td>
<td>0.0004</td>
<td>0.0155</td>
<td>0.0121</td>
</tr>
<tr>
<td>Kuta Gugung</td>
<td>0.0006</td>
<td>0.0135</td>
<td>0.0223</td>
<td>0.0015</td>
<td>0.1232</td>
<td>0.0003</td>
<td>0.0132</td>
<td>0.0131</td>
</tr>
<tr>
<td>Kuta Rayat</td>
<td>0.0006</td>
<td>0.0176</td>
<td>0.0231</td>
<td>0.0017</td>
<td>0.1442</td>
<td>0.0003</td>
<td>0.0143</td>
<td>0.0113</td>
</tr>
<tr>
<td>Kuta Tunggal</td>
<td>0.0008</td>
<td>0.0177</td>
<td>0.0285</td>
<td>0.0017</td>
<td>0.1375</td>
<td>0.0007</td>
<td>0.0186</td>
<td>0.0142</td>
</tr>
<tr>
<td>Gamber</td>
<td>0.0008</td>
<td>0.0185</td>
<td>0.0273</td>
<td>0.0018</td>
<td>0.1653</td>
<td>0.0006</td>
<td>0.0187</td>
<td>0.0141</td>
</tr>
<tr>
<td>Mardinding (lake)</td>
<td>0.0006</td>
<td>0.0143</td>
<td>0.0262</td>
<td>0.0020</td>
<td>0.1402</td>
<td>na</td>
<td>0.0132</td>
<td>0.0121</td>
</tr>
<tr>
<td>Sukameriah (lake)</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Batu karang</td>
<td>0.0005</td>
<td>0.0021</td>
<td>0.0198</td>
<td>0.0282</td>
<td>0.0412</td>
<td>0.0007</td>
<td>na</td>
<td>0.0189</td>
</tr>
<tr>
<td>IGR</td>
<td>1</td>
<td>0.01</td>
<td>0.03**</td>
<td>0.02**</td>
<td>0.5*</td>
<td>0.01*</td>
<td>0.02</td>
<td>1*</td>
</tr>
</tbody>
</table>

IGR: Indonesian Government Regulation; na: not analysis; ns: no sample

*Based on IGR (Permenkes No 416/Menkes/Per/IX/1990);
**IGR for fisheries and livestock water
***IGR for agricultural water

Heavy metals concentration in soils are shown in Table 5. Result indicate that all location which soil covered by volcanic ash were found Pb, Zn, Mn Cu and Fe. The highest concentration of Pb, Zn, Mn, Cu and Fe (53.05, 37.90, 28.22, 1.17 and 11.10) mg/kg respectively was obtained at sampling location of Kuta Rayat, Sigarang-garang, Sukameriah, Gamber, Kuta Rayat villages respectively (radius 3 - 4 km from eruption center) and a minimum of (0.10, 15.15, 10.15, 0.35 and 5.50) mg/kg respectively at sampling location Batu Karang, and Mardinding respectively (radius ± 7 km from eruption center). The higher concentration of Pb, Mn and Fe may be attributed to the contribution of volcanic ash which covered the soil. Nevertheless, concentration of As, Cd, Pb and Zn in soil at all sampling location did not exceed the PTE-MPC (CEPA, 1995).
Table 5. Heavy metal concentration in soil samples

<table>
<thead>
<tr>
<th>Sampling locations</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
<th>Mn</th>
<th>Se</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sukatepu</td>
<td>bdl</td>
<td>bdl</td>
<td>0.10</td>
<td>18.07</td>
<td>10.25</td>
<td>na</td>
<td>0.40</td>
<td>6.50</td>
</tr>
<tr>
<td>Sukanalu</td>
<td>bdl</td>
<td>bdl</td>
<td>0.18</td>
<td>30.22</td>
<td>25.10</td>
<td>na</td>
<td>0.86</td>
<td>7.15</td>
</tr>
<tr>
<td>Sigarang-garang</td>
<td>bdl</td>
<td>bdl</td>
<td>0.16</td>
<td>37.90</td>
<td>20.15</td>
<td>na</td>
<td>1.07</td>
<td>5.80</td>
</tr>
<tr>
<td>Kuta Gugung</td>
<td>bdl</td>
<td>bdl</td>
<td>0.23</td>
<td>28.10</td>
<td>15.20</td>
<td>na</td>
<td>0.67</td>
<td>6.70</td>
</tr>
<tr>
<td>Kuta Rayat</td>
<td>bdl</td>
<td>bdl</td>
<td>53.05</td>
<td>25.35</td>
<td>18.15</td>
<td>na</td>
<td>0.55</td>
<td>11.10</td>
</tr>
<tr>
<td>Kuta Tunggal</td>
<td>bdl</td>
<td>bdl</td>
<td>0.20</td>
<td>20.50</td>
<td>20.16</td>
<td>na</td>
<td>0.61</td>
<td>10.14</td>
</tr>
<tr>
<td>Gamber</td>
<td>bdl</td>
<td>bdl</td>
<td>0.13</td>
<td>28.00</td>
<td>20.18</td>
<td>na</td>
<td>1.17</td>
<td>8.80</td>
</tr>
<tr>
<td>Mardinding</td>
<td>bdl</td>
<td>bdl</td>
<td>1.50</td>
<td>20.15</td>
<td>10.15</td>
<td>na</td>
<td>0.45</td>
<td>5.50</td>
</tr>
<tr>
<td>Sukameriah</td>
<td>bdl</td>
<td>bdl</td>
<td>2.60</td>
<td>27.50</td>
<td>28.22</td>
<td>na</td>
<td>1.15</td>
<td>9.70</td>
</tr>
<tr>
<td>Batu Karang</td>
<td>bdl</td>
<td>bdl</td>
<td>0.10</td>
<td>15.15</td>
<td>10.15</td>
<td>na</td>
<td>0.35</td>
<td>6.70</td>
</tr>
<tr>
<td>PTE-MPC*</td>
<td>30</td>
<td>0.3</td>
<td>300</td>
<td>250</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

*PTE-MPC*: "Maximum permissible concentrations of potential toxic elements" for agricultural soils of China (CEPA, 1995)

bdl: below detection limit (detection limit 0.01 ppm); na: not analysis; nd: no data

**Conclusion**

The result from water samples showed that the concentration of Cd (in Sukatepu, Sukanalu, Sigarang-garang, Kuta Gugung, Kuta Rayat, Kuta Tunggal, Gamber and Mardinding villages) and Zn (in Mardinding and Batu Karang villages) were higher than the standard concentration for fisheries and livestock water (Indonesian Government Regulations No. 20, 1990) of 0.02 mg/L. Result indicate that all location which soil covered by volcanic ash were found Pb, Zn, Mn, Cu and Fe. Concentration of As, Cd, Pb and Zn in soil at all sampling location did not exceed the PTE-MPC (CEPA, 1995).

**Acknowledgment**

The authors would like to express their gratitude to Dr. Prihasto Setyanto, director of IAERI, and their staff for their assistance, support and encouragement.
References


Heavy Metals in Agricultural Soil and Using Plants to Clean up Contaminated Soils (Phytoremediation) in Vietnam

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Abstract: Since the 1990s, Vietnamese agriculture has developed a stronger focus on food quality and safety, partly in response to negative impacts from the emerging industrial sector. Specifically, contamination by heavy metals led to a reduction in soil quality and soil health. Studies were consequently implemented to evaluate the heavy metal contents of agricultural soils and we report the results of a major study of copper (Cu), cadmium (Cd), lead (Pb) and zinc (Zn), in 6 types of agricultural soils. Though heavy metal contamination occurred at a local scale, in general, agricultural soils in Vietnam cannot be regarded as contaminated. Several projects aim to find solutions to clean up contaminated soils, especially by phytoremediation. As a result, some species of plants were found to be good absorbents of heavy metals in soils. They are: water morning glory, water hyacinth, cabbage, pineapple guava, vetiver grass, primrose willow, yellow sawah lettuce, okra, sweet leaf.

Key Words: copper (Cu), cadmium (Cd), lead (Pb) and zinc (Zn), soil types.

1. Introduction

Vietnam is a Southeast Asia country with a 33,095.1 km² of land area and over 1 million km² of sea territory with many islands. On the mainland, there are 26,280.5 km² of agricultural and plantation forest land, of which 10,151.1 km² is used for agriculture. Agriculture contributes about 20% of GDP and occupies about 50% of human resources.

As a tropical country, Vietnam enjoys many advantages for agricultural production. There are large plains in two parts of the country which are the main centers of agriculture. Located in the North, the Red River delta is also the root of Vietnamese culture. The Mekong River delta in the South is the bigger rice production area and the source of most of the exported rice. That is, alluvium is the most important type of agricultural soil in Vietnam; however, smaller areas of five other soil types are used, such as: grey soils degraded from alluvium, located in midland areas; ferralitic soils in mountainous areas; acid sulfate soil, mostly in the Mekong River delta; and saline coastal soil. These soils are important for local and regional food production.

From the late 1980s, industrial production has contributed increasingly to Vietnam’s economic development. Industry directly competes with agriculture for human, land and other natural resources. However, industry also indirectly affects agriculture, e.g. by contaminating soil with heavy metals; although, such contamination is usually restricted to small areas of land located near industrial sites. Nonetheless, increasing emphasis on food quality and safety requires identification of problem areas, and either their exclusion from production or their remediation. This paper describes aspects of the heavy metal content of agricultural soils in Vietnam and some attempts to phytoremediate contaminated soils.
2. Heavy metals in Vietnam’s agricultural soils

Several projects have investigated the scale of pollution of agricultural soils by heavy metals in Vietnam, the most recent being a study by the Soils and Fertilizers Research Institute, conducted from 2002 to 2007. The heavy metals measured were copper (Cu), cadmium (Cd), lead (Pb) and zinc (Zn). Soils (600-700) were sampled from all agricultural regions of Vietnam across the 6 soil types described in the previous paragraph. The 95% confidence intervals of the total metal concentrations found in the study are presented in Table 1.

Table 1. Concentrations of Cu, Pb, Cd and Pb in agricultural soils in Vietnam

<table>
<thead>
<tr>
<th>Soil types</th>
<th>Cu (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Zn (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>95% confidence interval</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alluvial</td>
<td>21.02-23.72</td>
<td>32.36-35.26</td>
<td>0.75-0.83</td>
<td>73.42-79.86</td>
</tr>
<tr>
<td>Grey degraded</td>
<td>8.37-10.75</td>
<td>13.56-16.74</td>
<td>0.37-0.42</td>
<td>20.34-25.36</td>
</tr>
<tr>
<td>Ferralitic</td>
<td>54.94-61.68</td>
<td>30.90-35.86</td>
<td>2.57-2.78</td>
<td>92.90-105.21</td>
</tr>
<tr>
<td>Active Acid Sulfate</td>
<td>23.63-25.94</td>
<td>36.51-40.01</td>
<td>0.94-1.00</td>
<td>66.12-73.75</td>
</tr>
<tr>
<td>Potential Acid Sulfate</td>
<td>21.50-25.93</td>
<td>31.00-35.78</td>
<td>0.94-1.09</td>
<td>73.63-88.78</td>
</tr>
<tr>
<td>Saline</td>
<td>38.45-45.36</td>
<td>42.54-46.82</td>
<td>1.09-1.27</td>
<td>80.90-86.04</td>
</tr>
<tr>
<td>Sandy</td>
<td>5.79-6.69</td>
<td>10.19-11.51</td>
<td>0.26-0.29</td>
<td>18.01-21.71</td>
</tr>
</tbody>
</table>

Table 2. Assessing levels for each metal in alluvial soils

<table>
<thead>
<tr>
<th>Assessments</th>
<th>Cu( mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Cd (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very low</td>
<td>&lt; 12.97</td>
<td>&lt; 22.74</td>
<td>&lt; 45.00</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Below average</td>
<td>12.97-22.37</td>
<td>22.74-33.81</td>
<td>45.00-76.64</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Above average</td>
<td>22.37-31.78</td>
<td>33.81-44.88</td>
<td>76.64-121.65</td>
<td>1.0-1.4</td>
</tr>
<tr>
<td>High</td>
<td>31.78-41.19</td>
<td>44.88-53.95</td>
<td>121.65-200</td>
<td>-</td>
</tr>
<tr>
<td>Very high</td>
<td>41.19-52.75</td>
<td>53.95-64.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Warning</td>
<td>&gt; 52.75</td>
<td>&gt; 64</td>
<td>&gt; 200</td>
<td>&gt; 1.4</td>
</tr>
</tbody>
</table>

The results in Table 1 were used to estimate thresholds and levels for each metal in each type of soil. The results for the most important soil type, alluvial, are shown in Table 2. That is, in alluvial soils, average levels of Cu, Pb and Zn are all above the grand means for all soil types, and Cd is below the average. Similar inferences apply to the heavy metals in other soil types, except Saline soils, where the concentrations of all the metals are above the grand means. The heavy metal concentrations are generally below those of concern; although there are some relatively small contaminated areas.

Furthermore, most of the Cu, Pb, Zn and Cd concentration are well below the maximum values mandated by Vietnam standard (QCVN 03:2008- National Technical Regulation on the Allowable Limits of Heavy Metals in Soils), i.e. Cu, Pb, Zn and Cd concentrations of 50, 70, 200 and 2 mg/kg dried soil, respectively. Although the corresponding USA and EU standards are lower than those of Vietnam, the contents are still under the USA and EU limits. Consequently, we can conclude that agricultural soils in Vietnam, in general, are not contaminated by Cu, Pb, Zn and Cd.

There is some literature on heavy metals in soils of local regions from the early part of the decade. Ho Thi Lam Tra (2000) found that the contents of Ni, Pb and Zn (total) in alluvial soils of the Mekong River delta are 18.6, 29.1 and 36.2 mg/kg, respectively. In addition, Vo Dinh Quang, (2001) reported heavy metal contents for alluvial soil of the Hoc Mon district of Ho Chi Minh City (Table 3).

Table 3. Contents of some heavy metals in soils from Hoc Mon district (mg/kg)

<table>
<thead>
<tr>
<th>Metals</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
<th>As</th>
<th>Hg</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowest</td>
<td>7.25</td>
<td>64.0</td>
<td>14.5</td>
<td>0.48</td>
<td>1.25</td>
<td>0.049</td>
<td>10.58</td>
</tr>
<tr>
<td>Highest</td>
<td>81.0</td>
<td>168.5</td>
<td>75.75</td>
<td>1.05</td>
<td>3.75</td>
<td>0.512</td>
<td>41.03</td>
</tr>
</tbody>
</table>
Nguyen Huu Thanh (2010) analyzed 120 soil samples in Hanoi and found about 50 samples to be contaminated by Zn compared with the Vietnam standard given above. Most of the contaminated soils were from Thanh Tri district, which is the topographically the lowest area of Hanoi, and affected by waste water from the city and from the Cau Buou industrial zone. The results also revealed a trend of decreasing heavy metal contamination with distance from the industrial sources. For example, a sample taken just 10 m from a metal factory had the highest Zn content (1,141 mg/kg). Other research implemented by Hanoi Agriculture and Rural development Department showed that 36 (of total 478) vegetable zones, with area of 932 ha, have been contaminated by heavy metals (mainly by Cd, Cu, Zn). Besides these zones, 108 sites (occupying 35.3 % of total area) did not meet the requirements of soil and irrigated water for safe vegetable production, with 77 having contents of heavy metals in irrigation water higher than allowable limits. Duong Tu Oanh (2006) stated that 8/10 soil samples in Tay Tuu village (Hanoi) were affected by Cd contamination, with concentrations exceeding 2 mg/kg. This is explained by the overuse of fertilizers, which contain high amounts of Cd, for flower cultivation. Nguyen Thi Lan Huang (2006) found some polluted sites in Hanoi suburban areas which were affected by industrial practices. Dang Thi An (2008) warned about the Zn/Pb pollution in some areas of Hich village (Thai Nguyen), where a Pb/Zn exploring and processing factory were located, and in Dong Mai village, which is a Pb recovery village.

In the South, there are also some warnings about Pb, Zn and Cd contamination in vegetable soils in the areas around Le Minh Xuan industrial zone in Binh Chanh, 12 districts, Ho Chi Minh City; Di An and Thuan An districts (Binh Duong province); Bien Hoa and NhonTrach districts (Dong Nai province).

3. Using plants to clean up contaminated soils (Phytoremediation) in Vietnam

Phytoremediation was first studied and applied in Vietnam 15 years ago. Tran Thi Tuyet Thu (2000) showed that water morning glory and water hyacinth were strong Pb accumulators and Ho Thi Lam Tra (2000) indicated that cabbage can accumulate an increased amount of Cd when the amount of applied sludge was increase. Diep Thi My Hanh (2000) investigated the Pb absorbing ability of many species, including: such asvine (Heterostremavillosum, L. Asclepiadaceae), capulin (Muntingiacalabura), vetiver (Vetiveriazizanoides Poaceae), and pineapple guava (Lantana camara L. Verbenaceae). Of these, pineapple guava was the most effective and there was a close correlation between Pb contents in the soil and the root. Chu Thi Ha, Nguyen Duc Thinh and Boudou Alain showed that the Cd and Hg contents of water hyacinth from the To Lich river was higher than that from the Nhue. Le Van Cat used some varieties of plants to separate As from water and after 6 days of filtering, the As content of the water fell by 10 µg/L. Vo Van Minh (2007) defined the ability of Vetiver to absorb Cd, Pb and chromium (Cr) from Khanh Son landfill, Bong Mieu landfill (from Bong Mieu gold mine) and Hoa Minh landfill, Lien Chieu district, Da Nang City. After 7 days, the contents of metals decreased by at least 46%. The project “Study application of plants to remedy heavy metal contaminated soils in mining zones”, led by Dang Dinh Kim, showed that two varieties of fern (Pteris vittata and Pittyrogramma calomelano), and goose grass (Eleusine indica), accumulated Pb, Zn, As and Cd. The grass Vetiver still grew well in soil containing 1,400–2,530 mg Pb/kg, which showed that it was highly tolerant of Pb. In the project “Study and select plants and micro bionism with high ability of heavy metals absorption and metabolism to clean up contaminated agricultural soil”, Le Nhu Kieu et al. selected several types of plants which accumulate Pb, Cu and Zn, such as fern, water-taro, nipa, butterfly needles and Alocasia. Primrose willow (L. Octovalvis spp. Octovalvis) accumulated 94.6 mg Cu/kg biomass, 1,690 mg Pb/kg biomass, and 178 mg Zn/kg biomass. Water spinach (Enydra fluctuans Lour) can accumulate 62 mg Cu/kg biomass, 1,140 mg Pb/kg biomass, and 198 mg Zn/kg biomass, Butterfly needles (Bidens pilosa. L.) accumulated 35.76 mg Cu/kg biomass, 900 mg Pb/kg biomass, and 112 mg Zn/kg biomass. Sunflower (Helianthus annuus) accumulated 37 mg Cu/kg biomass, 1,050 mg Pb/kg biomass, and 160 mg Zn/kg biomass.

Despite these results, there is still little uptake of sunflower to clean up soil contaminated by heavy metals. Tran Kong Tau (2005) studied the Cd and Zn absorption ability of 9 popular ornamental trees of Hanoi and stated that Suzi Daisy and Schefflera heptaphylla (L.), both highly accumulate Cd and Zn. After 20 days, Suzi daisy can contain 475 mg Zn/kg biomass.
The Soils and Fertilizers Research Institute carried out the project: “Apply biological methods to remedy heavy metal contamination in soil and water body of the vegetable special cultural areas in East Southern Vietnam and Mekong River delta”. The project identified 9 plant species that grow strongly on contaminated soils: holly mangrove (*Acanthus illicifolius*), yellow sawah lettuce (*Limnocharis flava*), custard-apple (*Annona reticulata*), water mimosa (*Neptuniaoleracea*), sweet leaf (*Sauropus androgynus*), okra (*Abelmoschus esculentus*), winged bean (*Psophocarpus tetragonolobus*), lotus (*Nelumbonucifera*) and carrot (*Daucus carota*). The data demonstrate that yellow sawah lettuce, okra, sweet leaf and winged bean can be used as multi-purposed plants to clean up heavy metal contaminated soil (Table 4).

Table 4. Contents of heavy metals accumulated in plant parts

<table>
<thead>
<tr>
<th>No</th>
<th>Plant</th>
<th>Part</th>
<th>Pb</th>
<th>Cd</th>
<th>As</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Holly mangrove</td>
<td>Root</td>
<td>1.048</td>
<td>0.044</td>
<td>1.15</td>
<td>0.073</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trunk</td>
<td>0.577</td>
<td>0.041</td>
<td>0.74</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaves</td>
<td>0.190</td>
<td>0.009</td>
<td>0.11</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Flower</td>
<td>0.495</td>
<td>0.007</td>
<td>0.56</td>
<td>0.005</td>
</tr>
<tr>
<td>2</td>
<td>Yellow sawah</td>
<td>Root</td>
<td>6.963</td>
<td>0.174</td>
<td>6.28</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>Lettuce</td>
<td>Trunk</td>
<td>0.890</td>
<td>0.081</td>
<td>1.10</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaves</td>
<td>0.377</td>
<td>0.028</td>
<td>2.93</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Flower</td>
<td>0.141</td>
<td>0.001</td>
<td>1.07</td>
<td>0.001</td>
</tr>
<tr>
<td>3</td>
<td>Custard-apple</td>
<td>Root</td>
<td>1.97</td>
<td>0.014</td>
<td>21.24</td>
<td>0.105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trunk</td>
<td>1.093</td>
<td>0.033</td>
<td>5.78</td>
<td>0.062</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaves</td>
<td>1.380</td>
<td>0.014</td>
<td>7.64</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fruit</td>
<td>0.387</td>
<td>0.003</td>
<td>7.41</td>
<td>0.008</td>
</tr>
<tr>
<td>4</td>
<td>Water mimosa</td>
<td>Root</td>
<td>0.465</td>
<td>0.009</td>
<td>0.65</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trunk</td>
<td>0.958</td>
<td>0.015</td>
<td>2.12</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaves</td>
<td>0.124</td>
<td>0.007</td>
<td>0.15</td>
<td>0.003</td>
</tr>
<tr>
<td>5</td>
<td>Sweet leaf</td>
<td>Root</td>
<td>1.528</td>
<td>0.008</td>
<td>12.94</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trunk</td>
<td>1.38</td>
<td>0.005</td>
<td>0.44</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaves</td>
<td>0.075</td>
<td>0.001</td>
<td>0.01</td>
<td>0.000</td>
</tr>
<tr>
<td>6</td>
<td>Okra</td>
<td>Root</td>
<td>2.826</td>
<td>0.481</td>
<td>10.17</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trunk</td>
<td>0.537</td>
<td>0.018</td>
<td>5.24</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaves</td>
<td>0.16</td>
<td>0.010</td>
<td>0.15</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fruit</td>
<td>0.112</td>
<td>0.004</td>
<td>0.062</td>
<td>0.000</td>
</tr>
<tr>
<td>7</td>
<td>Winged bean</td>
<td>Root</td>
<td>1.243</td>
<td>0.145</td>
<td>1.45</td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trunk</td>
<td>0.541</td>
<td>0.170</td>
<td>1.17</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaves</td>
<td>0.260</td>
<td>0.074</td>
<td>0.35</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fruit</td>
<td>0.081</td>
<td>0.004</td>
<td>0.22</td>
<td>0.000</td>
</tr>
<tr>
<td>8</td>
<td>Lotus</td>
<td>Bulb</td>
<td>3.23</td>
<td>0.120</td>
<td>12.99</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trunk</td>
<td>0.483</td>
<td>0.005</td>
<td>6.28</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaves</td>
<td>0.16</td>
<td>0.032</td>
<td>2.91</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fruit</td>
<td>0.123</td>
<td>0.001</td>
<td>0.40</td>
<td>0.000</td>
</tr>
<tr>
<td>9</td>
<td>Carrot</td>
<td>Bulb</td>
<td>0.927</td>
<td>0.140</td>
<td>7.64</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trunk, leaves</td>
<td>0.402</td>
<td>0.003</td>
<td>0.59</td>
<td>0.005</td>
</tr>
</tbody>
</table>
4. Conclusion

Industrial development has encroached on agricultural land in Vietnam and caused heavy metal contamination. There are also problems caused by the persistent application of large amounts of chemical fertilizers. Nonetheless, excessive contamination is restricted to local areas close to industrial zones; consequently it can be said that Vietnam does not have a big problem with agricultural soil quality.

Despite this fact, there is considerable concern about the future based on the rapid pace quick of industrial development and the intensification of chemical fertilizer applications. This concern has led to studies to identify plants that are tolerant to and take up high concentrations of contaminants for use in phytoremediation. A number of suitable plants have been identified, but to our knowledge, remediation has not been attempted at the paddock scale. Cost aside, part of the reluctance to apply phytoremediation may be that there is no organized method to safely dispose of the contaminated plant material once it is harvested. This is a policy area that needs to be addressed.

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Land Use and Land Degradation Situation in Cambodia, and Possible Solutions

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Abstract: The Cambodian economy is largely based on agriculture and most of the population is living in the rural area depending on agricultural activities. Agricultural production is mainly concentrated in the northwestern areas; in the central plains of Tonle Sap Lake and Mekong rivers; and in the north and northeastern areas. Our people consider land/soil is a key factor among other inputs and services for sustainable agricultural production. The estimated total land-use area for agriculture is about 4.37 million ha. Rice is the dominant crop, comprising of about 1.0 million ha, comprises mainly of rubber, field crops and fruit trees. Cambodia is now facing with the ever challenge “poverty and environmental degradation”. Land degradation found many forms and caused mainly by human-induced activities and natural factors as it negatively impacts the environment, agricultural production so as to impact food security, social and economical development. To address this challenge, our government and people efforts are committed to combat land degradation, strengthen food production and to alleviate poverty. The complex nature of the causes of land degradation, together with policy reforms in the agriculture and natural resources management sectors, have stimulated many stakeholders to generate national and local solutions to problems by formulating various legal, institutional and technical frameworks, including research and development, and extension tools and services. The dearth of updated knowledge about land resources and its management, and lack of policy instruments have been ones of the major constraints on the productive and sustainable use of agricultural lands. In response to the current land uses and land degradation situation, the legal and institutional frameworks have to be soon finalised and effectively enforced, and the technical frameworks that already identified some prioritized actions need to be urgently researched and implemented to better manage agricultural lands, forest, water and biological resources, as well as for better strengthening governance and financing aimed at providing benefits to the country and people.

Keywords: Cambodia agriculture, land use, land degradation, solutions

1. Introduction

Cambodia is a tropical country located in the peninsula of mainland Southeast Asia with a land area of 181,035 km², in which 171,515 km² is land and 4,520 km² is water. On the south and the west is the gulf of Thailand with the coastline of 435 km. The land border of 2,438 km runs along Thailand on the west, Vietnam on the east and Lao PDR on the north. Of the 23 provinces and one municipality, there are 159 districts, 26 towns, 8 khans, and 1,417 communes (MoP, 2010).

Cambodia is an agrarian society with population of 14.5 millions. About 80% of the population lives in rural areas (MoP, 2012), and is engaged in agricultural activities of which the majority is subsistent small holder farm, depending largely on the rainfed lowland rice farming for the livelihood, including 49% in the central lowlands region along the Mekong River, 33% around Tonle Sap Lake, 7% around the coastal zones and 11% in the high land or plateau areas (SAW, 2010).

Table 1. Average rainfall (mm) and temperature (°C) between 2005 and 2009

<table>
<thead>
<tr>
<th>No.</th>
<th>Region Description</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Coastal region</td>
<td>1,777</td>
<td>2,453</td>
</tr>
<tr>
<td></td>
<td>Rainfall</td>
<td>24.1</td>
<td>31.8</td>
</tr>
<tr>
<td>2</td>
<td>North of Tonle Sap region</td>
<td>1,391</td>
<td>1,757</td>
</tr>
<tr>
<td></td>
<td>Rainfall</td>
<td>23.4</td>
<td>32.9</td>
</tr>
<tr>
<td>3</td>
<td>South of Tonle Sap region</td>
<td>1,207</td>
<td>1,886</td>
</tr>
<tr>
<td></td>
<td>Rainfall</td>
<td>22.2</td>
<td>35.0</td>
</tr>
<tr>
<td>4</td>
<td>East of Mekong region</td>
<td>1,389</td>
<td>1,777</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>23.6</td>
<td>39.9</td>
</tr>
</tbody>
</table>

Cambodia’s climate is governed by monsoons, and is characterized by two distinct seasons i.e. rainy or wet, and dry. The rainy season starts from May to October, with strong prevailing winds, from
the southwest together with heavy rains and high humidity. The dry season starts from November to April with light winds and low humidity. The humidity level changes from 60 to 80%. The climate changes with elevation which can be classified into four regions. The average annual rainfall and maximum and minimum temperatures which were recorded between 2005 and 2009 in those regions are listed in Table 1.

When the volume of water coming from the Mekong River increases, the water collected in the Tonle Sap Lake via the Tonle Sap River, also enlarging the lake four-fold. Therefore, apart from providing environment services and serving as potential reservoir for irrigation, the lake also acts as flooding flood prevention control measure during rainy season.

The land is generally flat in the central areas less than 50 m above seas level with mountainous (up to > 1000 m asl), the highest mountain in SW (Oral): 1813 m asl, and upland areas in the southwest, the east and the northeast.

Cambodia has embraced the principles of democracy and free enterprise and seeks full integration into the world economy and is now moving beyond post-conflict into a period of steady economic development. With the return of peace and the restoration of macroeconomic stability after the 1993 general election, the country has had the opportunity to achieve far-reaching reforms in all facets of economic and social life, and in particular, raises living standards of its citizens, who in the past have been receiving the lowest income in the world (MoP, 2010). A study conducted by the World Bank has classified Cambodia in the top 10 developing countries with the highest economic growth rate between 1998 and 2007 with the average annual growth rate of 2 digits (World Bank, 2009). Twenty five percent (25%) of the population live under the poverty line and the GDP per capita was 792 USD in 2010, and now is approximately 1,000 USD (MoP, 2013).

The agriculture sector remains the country’s main economic driver accounting for about 30% of GDP in 2001-2009. The agricultural growth was achieved at 4.3 percent in 2012, comparable to the 2011 and 2010 growth rates of 3.1 percent and 4.0 percent, respectively. Its contribution to the real GDP growth, 15.0% in 2012 compared to 11.3% in 2011 and 18.3% in 2010, becomes smaller while the growth of the tourism and industry sector has increased remarkably in the last 3 years (Ly and Enrique, 2013). However, the sustained growth of agricultural sector helps to secure the healthy growth of national economy as the other two sectors depend importantly on external environment, which remains fragile. The agriculture provides more than 60% of the total employment in the country. The government's rectangular strategy seeks to improve the sector further by highlighting four important approaches; agricultural productivity and diversification, land reform, fishery reform, and forestry reform.
The progress in the agriculture sector is fundamental to the poverty reduction, and contribution to GDP growth and macro-economic stability. The development of all the sub-sectors, together with equitable land allocation and management, measures to address the challenges and problems, prevention and suppression on illegal land grabbing, has been successfully carried out. At the same time, the Royal Government of Cambodia (RGC) has also made a lot of efforts to strengthen close cooperation with its development partners to mobilize resources to promote agricultural productivity to ensure food security and to contribute to supply the products to local and international markets.

Table 2. Rice production in Cambodia from 2009-13

<table>
<thead>
<tr>
<th>Description</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
<th>Change 2013/2012 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cultivated Areas (ha)</td>
<td>2,615,741</td>
<td>2,719,080</td>
<td>2,795,892</td>
<td>2,968,529</td>
<td>3,007,545</td>
<td>1.31%</td>
</tr>
<tr>
<td>Harvested Areas (ha)</td>
<td>2,613,363</td>
<td>2,674,603</td>
<td>2,777,323</td>
<td>2,766,617</td>
<td>2,980,297</td>
<td>7.72%</td>
</tr>
<tr>
<td>Rice Yield (t/ha)</td>
<td>2.746</td>
<td>2.836</td>
<td>2.970</td>
<td><strong>3.173</strong></td>
<td><strong>3.117</strong></td>
<td>-1.76%</td>
</tr>
<tr>
<td>Production (mt)</td>
<td>7,175,473</td>
<td>7,585,870</td>
<td>8,249,452</td>
<td>8,779,365</td>
<td>9,290,940</td>
<td>5.83%</td>
</tr>
<tr>
<td>Rice Surplus (mt)</td>
<td>2,025,033</td>
<td>2,244,598</td>
<td>2,516,752</td>
<td>2,780,328</td>
<td>3,031,017</td>
<td>9.02%</td>
</tr>
<tr>
<td>Paddy Surplus (mt)</td>
<td>3,164,114</td>
<td>3,507,185</td>
<td>3,932,425</td>
<td>4,344,263</td>
<td>4,735,964</td>
<td>9.02%</td>
</tr>
</tbody>
</table>

Source: MAFF, 2014

Ministry of Agriculture, Forestry and Fisheries (MAFF) promoted all forms of agricultural production, especially for strategic crops, such as rice, rubber and subsidiary crops, and animal husbandry and fishing, not only to meet local food demand but also to obtain a surplus for exportation (MAFF, 2010). At the time that world food crisis and world economic downturn persisted, Cambodia put much of its efforts in and was able to increase food production to overcome the challenges, particularly through the expansion of rice production and the produce export promotion, to contribute to increased local people's livelihoods and accelerate the pace of poverty reduction.

The Agricultural Sectoral Development Plan 2009-2013 (MAFF, 2010a) defined its long-term vision that “To ensure enough and safe food availability for all people, reduce poverty, increase GDP per capita and sustainable natural resource management conservation”. Between 2012 and 2013, the average paddy yields of 3.17 t ha\(^{-1}\) and 3.11 t ha\(^{-1}\) in 2012 and 2013 were reported (Table 2). The average yield in 2012-13 was the highest for the country’s history so as to make the total production to 9.29 million tons (MAFF, 2014).

Table 3. Cambodian major agricultural commodities production from 2005-13

<table>
<thead>
<tr>
<th>Commodities</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maize</td>
<td>90,732</td>
<td>108,836</td>
<td>142,391</td>
<td>163,106</td>
<td>206,058</td>
<td>213,622</td>
<td>174,257</td>
<td>216,330</td>
<td>239,748</td>
</tr>
<tr>
<td>Cassava</td>
<td>30,032</td>
<td>97,918</td>
<td>108,122</td>
<td>179,945</td>
<td>160,326</td>
<td>206,226</td>
<td>391,714</td>
<td>361,854</td>
<td>421,375</td>
</tr>
<tr>
<td>Mungbean</td>
<td>60,570</td>
<td>85,140</td>
<td>65,261</td>
<td>45,605</td>
<td>49,599</td>
<td>69,206</td>
<td>68,111</td>
<td>66,850</td>
<td>54,312</td>
</tr>
<tr>
<td>Soyabean</td>
<td>118,760</td>
<td>75,053</td>
<td>76,981</td>
<td>74,413</td>
<td>96,388</td>
<td>103,198</td>
<td>70,584</td>
<td>71,337</td>
<td>80,688</td>
</tr>
<tr>
<td>Total 4 crops</td>
<td><strong>300,094</strong></td>
<td><strong>366,947</strong></td>
<td><strong>392,755</strong></td>
<td><strong>463,069</strong></td>
<td><strong>512,370</strong></td>
<td><strong>592,250</strong></td>
<td><strong>704,666</strong></td>
<td><strong>716,370</strong></td>
<td><strong>796,123</strong></td>
</tr>
</tbody>
</table>

Source: MAFF, 2014
In general, the cultivated areas for subsidiary and industrial crops are fluctuated, according to the market demand. The production areas of 4 main crops (maize, cassava, mungbean and soybean) was yearly increased from 300,094 ha in 2005 to 796,123 ha in 2013 (+165%), (Table 3). According to MAFF report 2013-2014 indicated that the cultivated areas of subsidiary and industrial crops in 2012 are also increased to 0.91 ha, and the total production is also shown to increase from 9.93 million tons in 2011 to 10.85 million tons in 2012 (+10%). Therefore, the total areas planted crop commodities are 4.39 million ha; to rice 3 million ha, fruit trees 0.19 million ha, rubber tree 0.28 million ha and 0.912 million ha to subsidiary and industrial crops (MAFF, 2014).

The human community is now facing with the biggest ever challenge in its history, “poverty and environmental degradation”. Every day, the number of choices to save the planet diminishes as the population continues to increase and overexploit the global environment. Until this 21st century, desertification and land degradation are still the global challenges as they negatively impact the environment, agricultural production so as to impact food security, social and economical development as well as the quality of life.

In the Kingdom of Cambodia, million of people live below poverty line and depend entirely on natural resources which are continuously decreased both in quantity and quality. Between 1965 and 2010, forest cover in the country decreased by 16.1% and the pace of deforestation between 2002 and 2010 is 0.52% per year (FA, 2010). The reduction has deteriorate nest of biodiversity, forest resources and value of their use in the future as well as to cause soil erosion under the influence of rainfall that eroe top fertile soil from upland to lower lands for the first few years so as to make the rest soil degraded. In the later years, agricultural landscapes are affected by high sedimentation, rocks and sand caused by water run-off, which contributes to low productivity (Tan and Phon, 2010). Therefore, if there is no effective prevention, this situation will cause land degradation in areas that use to be forests and in low-lying land areas and it will ultimately cause the land to lose all of its agricultural productivity capability. To address this challenge, our government and people are committed to the Millennium Development Goals, including the overarching goal of halving poverty by the year 2015. But so far, most of our efforts to combat land degradation and to alleviate poverty still remain fragmented and inadequately concerted.

The United Nations Convention to Combat Desertification (UNCCD), which Cambodia became a signatory member on October 15, 1994 and ratified on August 13, 1997, has given new hope for the problems. To comply with its obligation, RGC with MAFF as the focal point has always participated in implementing activities described in the convention and decided by the conferences of the convention. Cambodia has participated in different activities to combat desertification, especially to prepare the National Action Plan (NAP) which reflects the willingness and commitments in protecting natural resources and cooperating with the nations in the region and the world. Given that the NAP cuts across many sectors, this instrument provides a framework of partnerships that calls for all government structures, communities and their leaders, NGOs and the private sector to work together and for the international community to help provide the necessary knowledge, capacity development and financial resources. The NAP has identified some priority actions that need to be implemented urgently to better manage land, forest, water and biological resources as well as for better strengthening governance and financing aimed at providing benefits to the country and people.

2. Agricultural land use
The soils of Cambodia developed in humid to sub-humid tropical climatic conditions with alternate wet-dry seasons of six-month duration. The soils are very diverse. The soil potential varies greatly ranging from very good to very poor. Cambodian soil of upper layer has been created by the decaying of mother rocks caused by acid recently or silt sedimentation for very long time (Crocker, 1962; Pheav et al., 1996; White et al., 1997).

It was reported that the first soil study related scientific work in Cambodia commenced at mid of the century. Saeki et al. (1959) were the first workers to conduct a detailed and specific survey of the chemical properties of the soils in main agricultural production areas of Cambodia.
Table 4. General characteristics of Cambodian soil potentials

<table>
<thead>
<tr>
<th>Fertility potential</th>
<th>Main soil groups (Crocker, 1962)</th>
<th>Areas (ha)</th>
<th>Areas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td></td>
<td>17,930,826</td>
<td>100</td>
</tr>
</tbody>
</table>

Source: Crocker (1962)

At the beginning of the 1960s, first classification of soil in Cambodia was made under the leadership of an American soil scientist named C.D. Crocker (1962). The soil was classified into 16 groups, a soil map with a scale of 1:1,000,000 was produced (Fig. 2), and some unknown soils were named that ordinary people (not soil scientists or experts) have a hard time understanding them. Since then, the work has been considered as the basis for evaluation of land or soil resources throughout the country. The study also found that the lands with high, medium and low potentials for agriculture are about 28%, 19% and 53%, respectively (Table 4).

Yasuo (1966) also attempted to develop a classification system by relating soil groups to agronomically important soil properties. His approach was promising but lacked accuracy and a precise soil group description, hence very general conclusions were drawn. Kawaguchi and Kyuma (1974) conducted a large survey of the paddy soils of tropical Asia soils including Cambodia. A pedo-morphological map at 1:1,000,000 was produced, the soils then were classified into 17 units based on the FAO guidelines and a soil map with the scale of 1:250,000 was produced. Most soil information was lost during a civil war 1975-1979. Till late 1990s, there was not much published information providing guidelines for soil use and management. In addition, there was no system to enable the simple recognition and communication about the different soils in the field.

A soil classification workshop was held 8-12 May 1995 in Phnom Penh to consider about rice soil classification in Cambodia. This gave a mandate for the development of a simple agronomically orientated soil classification. The Cambodian Agronomic Soil Classification System (CASC) was developed in the country to complement the first comprehensive soil taxonomy classification to improve the management and use in a broader scale of the country’s resources (White et al., 1997). CASC identified 11 Soil Groups in the main rice growing areas, and soils were mapped at 1:900,000 (Fig. 3).

Early 2000s with a project supported by JICA, conducted a country-wise agricultural land use and produced a map (JICA, 2002). Since 2003, land capability and suitability classification have been thoroughly studied for rice crop in the lowlands, but very little done for non-rice crop in the uplands (ACIAR, 2008). Land capability for field crops classified into five classes based on assessment of soil pH, nutrient availability, surface condition, surface soil structure, rooting depth, water logging, inundation, soil water storage, soil workability, water erosion risk, and phosphate export (Seng and White, 2006).

In 2010, agricultural land was about 24% while forest land was about 56% of the country’s total land area (Seng, 2010). The land used for agriculture was estimated in 2002 to be about 3.7 million ha excluding ELCs (Table 5). Major agricultural production zones are scattered in the northeaster region of the country, near to Thai border, low land around the Tonle Sap lake and other main rivers down to the Mekong and Basac rivers delta on the southern and south-eastern parts of the country. Those lands can be classified as lowland and upland.
1) Lowland

About 80% of lowlands, which is equivalent to 3.57 million ha, have been used for agricultural production. In these areas, rice is the dominant crop (2.72 million ha) which has been grown by farmers as wet-season, dry-season and deep-water rice crops. The soil potentials for the paddy fields were classified into three categories namely high, medium and low land potentials for the crop (White et al., 1997).

The lands with low potential such as Prateah Lang and Prey Khmer soils account for approximately 40% of the lowlands. Bakan soil group is another soil with low potential. Soil groups with a medium potential are Tuol Samrong and Kampong Siem. Labansiek used to be the soil type with medium potential too, but it has not been used and managed well for both rice and other crop productions. Kampong Siem soil has the capacity to retain water for a long time as it has thick layer of clay. This soil is normally scattered on sloping areas so as to be very vulnerable to soil erosion. It has sufficient nutrients and pH with medium acid. Even it can be subjected to high risk of being very wet;
this soil type has the capacity to drain water out as long as the water table is not too close to the surface (ACIAR, 2008). Soils with high potential are Kien Svay, Krakor and Kbal Por groups.

2) Upland

Most of the crops grown in the upland areas are rubber, subsidiary and industrial crops (corns, soybeans, mungbean, peanuts, and sesames), fruit trees (orange, mango, and longan), cassavas, sweet potatoes and bananas, among others. The size of the upland areas is increased to about 1.40 million ha excluding ELCs (MAFF, 2014). Lanbansiek soil group have been well-known for its good potential (White et al., 1997) for rubber plantations. The land has the characteristics suitable for land preparation, crop growth and not easily degraded. Even this soil becomes clay when it is wet, its porosity can still allow for quick water draining after a rain event but retains sufficient water for crops. However, the bottom layer of the soil has very strong acidic reaction so as to cause some problems to the crop roots and growth.

Sandy soils have also been observed in the highland areas. They are scattered on the southern, south-eastern and northern parts of the country and around the Tonle Sap Lake (Noble and Seng, 2008). Recently, another soil group Oraing Ov, has been suggested to separate from Labansiek group (Seng and White, 2006). The first soil is on the slope areas scattered between Labansiek and Kampong Siem soils, so as to be not so vulnerable to flooding. Oraing Ov soil is normally hard to plow and has lower quality than Labansiek soil due to the presence of stons and its limited capacity in retaining water.

Despite the awareness on the problems for sustainable use and management of the soils, especially on the need for knowledge on the components, and bio-physical characteristics of the soils, there has not been any clear study on assessment on land suitability and sustainable cultivation system available for improvement of agricultural sector in the future of the soils in the upland areas.

Table 5. Agricultural Land use categories in the Kingdom of Cambodia

<table>
<thead>
<tr>
<th>No.</th>
<th>Land use type</th>
<th>Land area (ha)</th>
<th>Percentage of total agricultural land</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Paddy fields</td>
<td>2,788,069</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>Paddy fields (Receding &amp; Floating)</td>
<td>194,864</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Paddy fields in villages</td>
<td>373,345</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>Other crop fields</td>
<td>260,145</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>Rubber plantations</td>
<td>84,758</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>Vegetable gardens</td>
<td>311,031</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>Fruit tree areas</td>
<td>8,179</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>8</td>
<td>Others (Slash &amp; burn)</td>
<td>349,636</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Total crop land (in 2007)</td>
<td>3,053,697</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Total unused land (in 2007)</td>
<td>1,316,330</td>
<td>30</td>
</tr>
</tbody>
</table>

Note: Total agricultural land in Cambodia is 4,370,027 ha which is equivalent to 24% of the country’s surface area (Seng, 2010).

3. The Problem on Soil and Water Resources Degradation in the Country, their Extent, Causes and Distribution

Land degradation (LD), as described by the United Nations Convention on Combating Desertification (UNCCD)-World Overview of Conservation Approaches and Technologies (WOCAT), takes many forms and is the result of different, inter-related causes such as: soil erosion by nature (by wind and water), inappropriate agricultural practices, deforestation, loss of biodiversity as well as natural disasters caused by climate change (UNCCD, 2006; WOCAT, 2006; WOCAT 2007). Land degradation is the persistent decrease in the supply of ecosystem goods and services as a result of changes in soil or vegetation, and is used here to include deforestation and the effect of climate change (drought and floods). Land degradations are also caused by the combination of social, economical,
political and natural factors which are different for different places. The causes of land degradation mainly are inappropriate land use practices (ISRIC, 1997). Douglas (2006) indicated that land degradation occurred in many parts of South-east Asia including Cambodia. Land degradation caused by nature and human activities, have taken place in different forms for different landscapes and soil types. The main forms of land degradation in Cambodia are soil degradation, deforestation, and the subsequent loss of biodiversity (Tan and Phon, 2010).

1) Natural disaster and climate change impacts

At least two factors exacerbate the effects of land degradation in Cambodia. One is the inherent low soil fertility in large portions of agricultural lands which has been reported as early as 1960’s (Crocker, 1962). Related to this is the natural limitation of most soils to retain water which tends to limit the organic matter content of soils, thereby contributing to low soil fertility.

Another exacerbating factor would be the effects of natural disaster risk and climate change, primarily through the increasing intensity and frequency of disasters such as floods and drought. Because of heavy rainfalls during the wet season and the usual flooding pattern from the Mekong river, Cambodia’s lowland areas experience floods every year. The extent of the flood varies from year to year, but normally the areas affected are up to 4 million ha (MRC, 2004).

Soils in large areas have poor water holding capacity. Delayed and insufficient rain, combined with the occurrence of a small dry season within wet season, has induced droughts in the wet and dry seasons. A succession of droughts and floods cause land degradation and considerable economic losses. Floods and droughts are considered to be the most dominant forms of extreme climate events. In 2008, at least 700 communes (50% of the total number of communes) were considered to be vulnerable to climate change. Most of these floods occurred on low lying provinces of the south and southeast as well as in upland areas in the northwest.

It has been considered further that climate change can induce land degradation because of the prolonged and increased frequency of droughts and floods. Rapid fluctuation of atmospheric temperature has also reduced the quantity and quality of land cover crops, underground water sources and the soil quality (Eswaran et al., 2004). The trends of present climate change have been shown by continuous temperature rise, the change of amount of rainfall and duration of floods and droughts.

In the past few years, due to the effect of climate change, it was observed that the amount of rainfall during the wet season has increased, while the amount of rainfall in dry season has decreased. Table 6 elaborates average amount and number of days with rainfall in four provinces as representative to different regions in Cambodia. These are: Coastal region (Kampot), northern part of Tonle Sap Lake (Siem Reap), Eastern part of Mekong River (Stung Treng), and southern part of Tonle Sap Lake (Takeo, Kandal, and Kampong Speu).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rainfall, mm</td>
<td>Days of rain</td>
<td>Rainfall, mm</td>
</tr>
<tr>
<td>Kampot province</td>
<td>1,790.9</td>
<td>181.6</td>
<td>2,085.8</td>
</tr>
<tr>
<td>Siem Reap province</td>
<td>1,440.7</td>
<td>141.8</td>
<td>1,469.5</td>
</tr>
<tr>
<td>Stung Treng province</td>
<td>1,865.9</td>
<td>139.8</td>
<td>1,647.5</td>
</tr>
<tr>
<td>Phnom Penh</td>
<td>1,324.7</td>
<td>123.8</td>
<td>1,461.9</td>
</tr>
</tbody>
</table>

Source: MoWRAM (2010)

Conventions related to environment have been made with the purpose to more effectively address global pressure on the environment which is threatening biodiversity and causing desertification. Climate change can be one of the root causes for desertification. For instance, with the
scarcity of water, lives on earth would hardly exist. At the same time desertification could make the climate change worse since it causes the increase in temperature and the decrease in rainfall.

Theoretically, the difference in maximum and minimum temperatures of less than 13°C is suitable for plant and other living things. In Siem Reap, Stung Treng and Phnom Penh, the difference of more than 17°C has been observed (Table 7) which can make serious change to ecological system.

Table 7. Temperatures (°C) recorded in 4 places represent different regions of Cambodia

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
<td>Diff</td>
</tr>
<tr>
<td>Kampot province</td>
<td>20.0</td>
<td>33.2</td>
<td>13.2</td>
</tr>
<tr>
<td>Siem Reap province</td>
<td>16.5</td>
<td>36.0</td>
<td>19.5</td>
</tr>
<tr>
<td>Stung Treng province</td>
<td>17.6</td>
<td>36.3</td>
<td>18.7</td>
</tr>
<tr>
<td>Phnom Penh</td>
<td>19.7</td>
<td>36.7</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Based on the strong evidence mentioned above, the preparation of NAP by proposing two major interventions are relevant to the agriculture sector is necessary for Cambodia:

1. Protection and restoration of forest cover in watersheds through reforestation and planting rubber, fruit trees etc., which provide the land with long-lasting cover and fertility; and
2. Soil conservation as well as soil improvement at the farm level using natural fertilizers such as composts and the cultivation of leguminous crops.

2) Human activities: In appropriate forest and land uses

The immediate causes of land degradation in Cambodia are inappropriate forest use and agricultural land use practices. Inappropriate land use practices are in turn influenced by such factors as population growth; urbanization; land tenure security and resources access by land users; the influence of prices and markets; the adequacy of regulations and enforcement; and availability of technical support to guide land users.

2.1) Loss of forest cover

The reduction of cover and quality of forest has impacted its capacity in providing social, economic and ecological services to society. The change in forest cover leads to change in biodiversity as well as decline of richness of forest resources and value of their future use. The change of forest cover, especially on sloping areas, leads to soil erosion of the upper layer, causing nutrients to drift off to cover the land areas downstream in the early years. But, in the later years, agricultural landscapes are affected by high sedimentation of fine stones and sand caused by water run-off, which contribute to low agricultural productivity. If there is no effective preventive measure, this situation will cause land degradation in both the areas that used to be forests and lowland areas, and will ultimately cause the agricultural land to lose all of its productivity.

Before the civil war in 1970s, based on the definition of FAO which considers vegetation cover on land from 10% and 0.5 ha, Cambodia has forest cover of approximate 73% (Table 8). But since 1993, as the vegetation cover needs to account from 20%, the interpretation of the forest cover has changed significantly. In theories, comparison of the data can not use different definitions of forest cover. However, (Table 9) shows that between 1965 and 2006, the forest cover areas decreased by about 16.1%, and the deforestation rate between 2002 and 2010 was about 0.52% annually (FA, 2010).
Table 8. Forest cover in 1965

<table>
<thead>
<tr>
<th>No.</th>
<th>Forest types</th>
<th>Areas</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ha</td>
<td></td>
</tr>
<tr>
<td>A.</td>
<td>Total Forest Land</td>
<td>13,227,100</td>
<td>73.04</td>
</tr>
<tr>
<td>1</td>
<td>Evergreen forest</td>
<td>3,955,300</td>
<td>29.90</td>
</tr>
<tr>
<td>2</td>
<td>Semi-evergreen forest</td>
<td>2,504,000</td>
<td>18.93</td>
</tr>
<tr>
<td>3</td>
<td>Dwarf evergreen</td>
<td>288,700</td>
<td>2.18</td>
</tr>
<tr>
<td>4</td>
<td>Deciduous forest</td>
<td>5,296,700</td>
<td>40.04</td>
</tr>
<tr>
<td>5</td>
<td>Coniferous forest</td>
<td>17,800</td>
<td>0.13</td>
</tr>
<tr>
<td>6</td>
<td>Bamboo forest</td>
<td>387,400</td>
<td>2.95</td>
</tr>
<tr>
<td>7</td>
<td>Flooded forest</td>
<td>681,400</td>
<td>5.15</td>
</tr>
<tr>
<td>8</td>
<td>Mangrove</td>
<td>38,300</td>
<td>0.29</td>
</tr>
<tr>
<td>9</td>
<td>Rear mangrove forest</td>
<td>57,500</td>
<td>0.43</td>
</tr>
<tr>
<td>B.</td>
<td>Non-Forest Land</td>
<td>4,883,400</td>
<td>26.96</td>
</tr>
</tbody>
</table>

Source: FA (2010)

Table 9. Change in forest cover between 1965 and 2010

<table>
<thead>
<tr>
<th>No.</th>
<th>Annual Evaluation</th>
<th>Forest Area</th>
<th>Non-Forest Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ha</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>1965</td>
<td>13,227,100</td>
<td>73.04</td>
</tr>
<tr>
<td>2</td>
<td>1992/93</td>
<td>10,859,695</td>
<td>59.82</td>
</tr>
<tr>
<td>3</td>
<td>1996/97</td>
<td>10,638,209</td>
<td>58.60</td>
</tr>
<tr>
<td>4</td>
<td>2002</td>
<td>11,104,293</td>
<td>61.15</td>
</tr>
<tr>
<td>5</td>
<td>2005/06</td>
<td>10,730,781</td>
<td>59.09</td>
</tr>
<tr>
<td>6</td>
<td>2010</td>
<td>10,339,826</td>
<td>56.94</td>
</tr>
</tbody>
</table>

Source: FA (2010)

Below is an elaboration of a number of key activities that are relevant to land size and forest quality reduction in the country.

a) Economic land concessions (ELCs)
In the desire to address the problem of deforestation, RGC has issued a policy for ELCs in line with different laws and regulations such as the Land Law which started to be effective in August 2001, Forest Law which started to be effective in August 2001, and Sub-decree on the land concession made in December 2005. In those, RGC:

1. Recognizes private sector as the important partner for the development of national resources through establishment of food and other commodity production zones;
2. Intends to reform agricultural system from small to large scale;
3. Promotes investment in agro-industry and attracts investment flow;
4. Increases people’s livelihoods through creation of jobs and increase of additional incomes;
5. Improves infrastructure, health and education services as well as marketing in the rural areas;
6. Promotes rubber and other tree plantations, animal production and aquaculture as well as processing for export, based on the principle of mutual appropriate benefits and the exchange or transfer of the production and processing technologies between the investors and state;
7. Reduces as much as possible the negative impact on the environment through implementation of different investment activities so as to maintain environmental, natural and development sustainability, etc.
From 1993 to May 2010, RGC has granted 142 companies which had the right to use ELCs for cultivation of agricultural and agro-industrial crops, forest and rubber trees, in the hopes that this action could help restore the forest cover and improve biodiversity. Since 43 of the companies did not follow the investment contracts, for instance they cleared the land and left it for several years without the forest cover so as to cause soil erosion and loss of biodiversity which ultimately led to land degradation, MAFF requested and received the government’s approval to terminate the principles and contracts as well as to confiscate land of 373,545 ha and to keep it back as national property. Therefore, there are 99 valid ELCs companies with a total area of 1,046,591 ha scattered in 17 provinces of Cambodia (MAFF, 2010b).

Due to the rapidly increasing need for agro-industrial lands and by facing a number of problems in the prevention of depleting natural resources, the government decided to convert the national protected areas of more than 640,000 ha that was under the responsibility of Ministry of Environment (MoE) to be managed by a number of private companies. We can conclude that land clearing and other investment activities of the companies supervised by MoE may seem to face with similar problems and to cause land degradation, if there is no close monitoring from technical institutions.

**b) Slash and burn agriculture**

Based on a policy analysis of agricultural land use and management that made by Seng (2010) was shown that slash and burn agricultural practice in some upland areas of Cambodia covers about 349,636 ha. For the last decade, this practice has led to the tendency in permanently owning the land which contributes to the loss of forest cover and cause land degradation.

**c) Clearing forest land for cultivation and to own the land**

Observing that a number of forests have been lost by clearing and burning to get the lands for cultivation and private ownership by some law violators. Provincial authorities have ordered with and without court warrant to confiscate land of 254,855 ha and 43,776 ha, respectively (FA, 2009a; FA, 2010). Without enough forest covers, these lands are now exposed to soil erosion.

**3) Other factors contributing to land degradation and sustainable land management**

Human activities that contribute to agricultural land degradation can be classified as direct and indirect including inappropriate agricultural practices, population growth, unclear land title, and low educational attainment as well as insufficient system for supporting services, institutions and governance.

**3.1) Socio-economic conditions**

Increasing the productivity and diversity of agriculture, mine clearing as well as the reforms of land, fisheries and forestry, have yet to reach their full potential (MoP, 2010). At present, agricultural lands are being threatened by the competition of other development sectors but on the other hand, the increase in the agricultural lands is also serious threat to the remaining forest lands. The biggest challenge for the country is the rapid increase of population that adds more pressure to the natural resources.

**3.2) Legal, policy, government responsibilities and institutional arrangements**

Other than supporting sustainable management of land and other resources, the legislations are also Cambodia’s contribution in the application of obligations mentioned in UNCCD, UNFFCC and UNCBD etc.

The existing legislations establishing land, water, and forests management and land use planning at the local level are important to anticipate, prevent and address the potential environmental effects that are caused by investment, mines exploitation, ELCs, etc. However, due to the insufficiency in monitoring the master plan for management and use ELCs as well as the lack of information on agricultural and not-agricultural land use zoning, deforestation and soil erosion keep continued.

When fully enforced, the above laws can help guide SLM. For instance, laws on natural resources provide basic zoning protocols e.g. classification of forests into production and protection forests. These laws also allocate resources to communities for them to help protect and use sustainably.
Cambodia needs to use its natural resources for its development and is, thus, promoting critical income generating industries such as mining as well as agribusiness through ELCs. To ensure the least disturbance on natural resources by these industries, three sets of regulations are important in implementing laws that involve the extraction of natural resources. These are the laws that (a) prescribe land use zones (e.g. protection vs. production forests etc.); (b) regulations governing business operations in particular sectors; and (c) the requirements for the conduct of EIA.

In practice, there is a major difficulty in enforcing laws relevant to SLM. Among the key deterrents is the lack of implementing guidelines (such as in the case of EIA) and insufficiency of resources to conduct compliance monitoring and guide land use operations of business operations.

Another constraint is the lack of inter-agency coordination. Commune land use planning (CLUP) is important for ensuring sound land use at the commune level. However, the participation of line agencies in the CLUP still needs to be strengthened to ensure that land use decisions of communes will be honoured by line agencies.

3.3) Role of women in SLM
Studies have shown that most of women have more tasks related to solving land degradation problems than men, since they are in direct contact with agricultural activities, both in and out of farms, while men mostly leave home for other jobs in urban areas (MAFF, 2008). Land degradation can cause high production cost but low in productivity and incomes. A study undertaken by the Ministry of Women’s Affair in 2004 discovered that there were women labours of 56% of farmers’ family members who are involved in traditional agriculture. On the other hand, among the workers for fee in agriculture, approximately 54% were women.

Therefore, in order to solve the land degradation problem effectively, attention has to be paid to increase the capacity and participation of women by setting up a rule for minimum number of woman extension workers and representatives in local committees for resources management. This has been stared already with the community forestry (CF) program.

Support programs have generally suffered from very low funding. Training programs for gender support need to be updated to incorporate new insights about the role of women in agriculture and environment. Gender focal persons are not very familiar with SLM concepts and principles although they profess high interest to learn about them.

3.4) Contribution of non-government organizations NGOs
Apart from RGC, many NGOs have also made lots of efforts to develop agriculture in the country. Among those, there are some NGOs involved in activities related to SLM.

There are significant numbers of NGOs working in agriculture development and NRM in Cambodia. Their roles have been recognized by the government as key development partners. Most of NGOs’ operations in Cambodia have close cooperation with RGC. Projects may either be "hands on" work with communities or monitoring and research. The above mentioned projects/programs which received grants from bilateral and multilateral funding agencies have been operating in cooperation with government counterparts.

3.5) Contributions of the private sector
The RGC established a “Government -Private Sector Forum” with committee for agriculture and agro-industry to manage solutions of different problems related to the agro-industry sector. The forum is also the mechanism for mobilizing financial resources and promoting contribution of private sector, in order to develop the agro-industry sector and SLM.

3.6) Contributions of Development Partners
The contributions of development partners in SLM particularly in agricultural landscapes is fairly recent compared to the longer history of investments in mainstream agricultural productivity improvement. Nonetheless, the assistance that have been made available, generated many technical and institutional innovations and best practices that can help guide future work in SLM. Such innovations are described in preceding sections as well as best practices described the in subsequent section are partly attributable to the technical and financial assistance made available.
3.4) Key trends of land degradation in Cambodian agricultural landscapes

The results of a study undertaken by a national consultant team led by Tan and Phon (2010) on causes of degradation of agricultural lands, which was completed in April 2010 indicated that land degradation caused by human activities have taken place in different forms for different landscapes and soil types (Table 10). The study focused on four selected sites including: (1) Pailin province—the issues of mining activities that cause soil erosion from upstream to downstream and changing agricultural practices; (2) Kampong Speu and Takeo provinces—the issues of deforestation in the upland areas (Oral mountain) which caused soil erosion to Stung Slakou and affects the paddy fields downstream (Samrong district, Takeo); (3) Kampong Cham—the issues of inappropriate land preparation and land management for agro-industrial crops including rubber and cassava on red soil; and (4) Svay Rieng—the issues of very acidic soil with low quality that should be improved.

Table 10. Key findings and recommendations on degradation of some agricultural lands

<table>
<thead>
<tr>
<th>Types of problems occurring</th>
<th>Examples of best practices</th>
<th>Possible mitigation strategies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Issue:</strong> Sandy soil and deforestation</td>
<td><strong>Study sites:</strong> Kampong Speu and Takeo provinces&lt;br&gt;. Lithosol in upstream will further erosion&lt;br&gt;Upstream soil erosion and downstream soil sedimentation&lt;br&gt;. Degraded forest in watershed areas and downstream sedimentation&lt;br&gt;. Scarcity of water in dry season&lt;br&gt;Land productivity reduced in downstream areas, e.g. affected Stung Slakou areas.</td>
<td>. Some good agricultural practices in Tram Kok district, Takeo province&lt;br&gt;. Planting multi-purpose forests in forest zones in Takeo Province</td>
</tr>
<tr>
<td><strong>Issue:</strong> Agricultural production in the upland area</td>
<td><strong>Site:</strong> Pailin and Battambang provinces&lt;br&gt;. Latosol soil type, which is prone to erosion in Pailin&lt;br&gt;. Plowing up and down the slope causing soil erosion and sedimentation in the downstream rice fields.</td>
<td>. Conservation efforts of Maddox Jolie Pitt project and CI and existing community forestry.</td>
</tr>
<tr>
<td><strong>Issue:</strong> Inappropriate agricultural practices.</td>
<td><strong>Site:</strong> Kampong Cham Province&lt;br&gt;. Latosol soil type with medium fertility&lt;br&gt;. Plowing up and down the slope, changing from strategic crop (rubber) to cassava&lt;br&gt;. Soil erosion, low fertilizer efficiency and compacted top soil (e.g. cassava plantation in Memot district and Chalong rubber plantation).</td>
<td>. Rubber Research Institute in Chop has piloted soil improvement using land cover crops.</td>
</tr>
</tbody>
</table>
Issue: Slash and burn agricultural practice  
Site: Mondulkiri province  
- Soil is prone to erosion  
- Slash and burn agricultural practices  
- Loss of biodiversity  
- Indigenous people live in small villages far away from each other.

<table>
<thead>
<tr>
<th>Issue:</th>
<th>Slash and burn agricultural practice</th>
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<tbody>
<tr>
<td>Site:</td>
<td>Mondulkiri province</td>
</tr>
<tr>
<td></td>
<td>Soil is prone to erosion</td>
</tr>
<tr>
<td></td>
<td>Slash and burn agricultural practices</td>
</tr>
<tr>
<td></td>
<td>Loss of biodiversity</td>
</tr>
<tr>
<td></td>
<td>Indigenous people live in small villages far away from each other.</td>
</tr>
</tbody>
</table>

| Pine tree and rubber tree plantations |
| Community Forestry is working to protect forest and biodiversity |
| Fruit trees and vegetable growing in some areas. |

Establishment of agricultural stations in the upland areas, like in Dalat, Vietnam, to determine methods to reduce the production cost and to grow vegetable suitable for the climate.

- Development of eco-tourism  
- Planting windbreak trees to prevent soil erosion by wind  
- Reforestation of the denuded mountains and hills  
- Practices suitable for land characteristics and alley cropping  
- Plant long-living trees on bare land.

Issue: Land degradation caused by natural factors  
Site: Svay Rieng province  
- Very acidic and toxic soil (Alumisol)  
- Scarcity of water in dry season  
- Farmers use lots of groundwater, synthetic fertilizers and pesticides for dry season rice.

| Selecting farmers for diversifying crops such as planting trees for firewood and fruits and aquaculture |
| Use bio-gas system and its residues |
| Demonstrating techniques to improve soil quality. |

Good water resources management  
- Appropriate application of chemical fertilizers  
- Encourage the use of agricultural residues for soil improvement  
- Less use of synthetic fertilizers containing S: (NH₄) SO₄.

Source: Tan and Phon (2010)

5) Impairment of watersheds

While Cambodia is a water abundant country, only 1% of the water is actually used. The agriculture sector consumes almost 60% of this 1%. The challenge is the low water retention capacity of the soil which provides too much water available in the wet season but too little water during the dry season (Johnston et al., 2013; de Silva et al., 2013).

In addition to Mekong river, there are other major tributaries such as Sesan, Sekong and Srepok rivers and Tonle Sap Lake which totals to 37 watersheds within the system. These watersheds would support 250 irrigation schemes serving approximately one (1) million ha of fields (Johnston et al., 2013; de Silva et al., 2013). Good quality watersheds can play very good roles in regulating water sources and groundwater. Watersheds can indirectly provide some services such as nutrient supply, flood regulation, and water purification. The productivity and sustainability of existing and newly proposed dams would also depend on these watersheds.

In 2004, Mekong River Commission classified various watersheds in terms of "risks to impairment". Three factors were considered: (1) degree of conversion of forests (within the watersheds) to non-forest use; (2) creation of new agricultural lands; and (3) ratio of lowland areas per capita within the watersheds (MRC, 2004). Based on these factors, at least 09 watersheds were considered to be in critical conditions and require close management attention (MAFF, 2010b).

Because of the impairment of watersheds, there was an observed increase in sedimentation in Tonle Sap Lake. It has been reported that 56% of irrigation schemes do not function fully because of sedimentation (MRC, 2004). Soil erosion especially due to inappropriate land use practices in
upstream creates a lot of sedimentation that also influence flooding. For instance, in the wet season of 1996, it was found that the sediment load in the Tonle Sap Lake, which flows from the Mekong river and other streams was two times higher than that of 1994. The maximum sediment load figure in this lake was 3,000 g m\(^{-3}\) in 1996 while in 1994 was only 1,500 g m\(^{-3}\) affecting flood storage capacity. Sedimentation combined with strong rainfall intensities due to climate change creates catastrophic floods in downstream areas (MRC, 2004). Furthermore, the increase and inappropriateness in synthetic fertilizer and pesticide applications in the areas around the Tonle Sap Lake has been believed to pollute the soils and damage the water quality in the Lake.

6) The challenges of governing groundwater
In the past decade, irrigation thus becomes an essential insurance protecting the farmer’s investment. Early wet season rice and especially dry season rice production are trending towards commercial production; most farmers growing dry season rice have larger holdings. To meet a need of water supply for crop intensification, individual pumping of groundwater use is widespread in the Mekong Delta and particularly in Svay Rieng and Prey Veng provinces of Cambodia where other sources of water are not available (Johnston et al., 2013). In general, groundwater is best used for supplementary irrigation, rather than full dry season irrigation, but regulating use is very difficult. Ministry of Water Resources and Meteorology (MoWRAM) has adopted a precautionary approach to groundwater use which is important because recharge systems and rates, as well as connections between surface and groundwater, are not well understood, and there can be considerable time lags before excessive extraction or pollution becomes evident.

Because there are trending a large number of individual users, and attributing pollution or over extraction to particular pumpers or polluters is difficult, enforcement of command-and-control approaches (e.g. licensing and metering) is impractical. Other less direct approaches exist, through economic instruments that use financial incentives and disincentives such as groundwater pricing, trading water rights or pollution permits, and subsidies and taxes. Another option is the introduction of voluntary policies, whereby users (often collectively) establish and enforce their own rules. de Silva et al. (2013) argues that voluntary compliance is the most practical approach since costs for monitoring and enforcing national legislation may become prohibitively high. Involving a wide network of actors, ranging from the private to public sectors, could lead to more effective and legitimate forms of groundwater governance in near future (Lopez-Gunn, 2009).


1) Previous and current programs, community practices and lessons learned
This section discusses the ideas and programs that have been considered and organized in Cambodia to address SLM. Information and experience from studies of the communities that participated in the conservation and protection of natural resources are also discussed.

1.1) Historical landmarks towards SLM oriented interventions
The road to SLM in Cambodia is characterized by the following milestones: during the Khmer empire, there are recorded soil and water management strategies that supported a thriving agricultural economy, development and implementation of policy to globalize agricultural economy and to add value to farmers’ products after the civil conflicts. As the consequence, the use of natural resources has increased.

The milestones in agricultural reform from the beginning of the 20\(^{th}\) century are:
1. Changing practice from producing only rice to crop diversification, the use of new and modern seeds that grow in shorter periods and provide with higher yields, the use of agricultural machineries and organic farming etc. to solve the problems of soil fertility;
2. Extension delivery systems and methodologies have been developed gradually in order to make farmers and other users adopt new information and technologies from "un directional" technology transfer paradigms to farming systems and agro ecosystems approaches;
3. Many debates have been made to raise the awareness and find ways to mitigate and adapt to the climate change.
For natural resources management:
1. The concept of community-based natural resources management has been introduced following the general trend in South East Asia. This was eventually followed by devolution reforms that involve transferring a number of authorities from the national to the local level;
2. Current discussions are looking for ways to establish mechanisms for protecting and managing forest such as the necessity for payments for environmental and ecosystem services, clean development, conservation concessions, privatization of small forest lots, and recreational urban forests;
3. Strengthening land administration systems has been started. These provide the mechanisms for recognizing, delineating and confirming land use rights and minimize conflicts over land resources management;
4. Very recently, RGC established the Environmental Impact Assessment (EIA) system which would provide the mechanism for scientifically determining the potential environmental impact of development projects that uses natural resources. The EIA system helps ensure that important land use and environmental standards are enforced.

1.2) Overview of current programs that address SLM

Table 11. RGC relevant policies and strategies as the basis for drafting laws and programs that support sustainable land management

<table>
<thead>
<tr>
<th>Description</th>
<th>Strategies and programs</th>
<th>Period covered</th>
</tr>
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<tbody>
<tr>
<td>National level land management</td>
<td>NSDP</td>
<td>2006 - 2010</td>
</tr>
<tr>
<td></td>
<td>Land management strategy</td>
<td>2009 - 2013</td>
</tr>
<tr>
<td></td>
<td>Policy announcement on governance, management and allocation of land</td>
<td>2009</td>
</tr>
<tr>
<td></td>
<td>Sub-decree on EIA</td>
<td>1999 - 2002</td>
</tr>
<tr>
<td>Local development plans</td>
<td>National program for democracy development in sub-national level</td>
<td>2010 - 2019</td>
</tr>
<tr>
<td>Lowland and upland agriculture</td>
<td>Strategy for agriculture and water</td>
<td>2006 - 2010</td>
</tr>
<tr>
<td></td>
<td>Agricultural sector development strategy (ASDP)</td>
<td>2006 - 2010</td>
</tr>
<tr>
<td></td>
<td>Master plan for national agricultural research</td>
<td>2006</td>
</tr>
<tr>
<td></td>
<td>Policy on the promotion of paddy production and rice export</td>
<td>2010 - 2015</td>
</tr>
<tr>
<td>Forest lands</td>
<td>Strategy for forest and environment</td>
<td>2007 - 2010</td>
</tr>
<tr>
<td></td>
<td>National forestry program (NFP)</td>
<td>2010 - 2030</td>
</tr>
<tr>
<td>Natural protected areas</td>
<td>Strategy for forest and environment</td>
<td>2007 - 2010</td>
</tr>
<tr>
<td></td>
<td>NBSAP</td>
<td>2002</td>
</tr>
<tr>
<td>Flooded forests and inland fisheries</td>
<td>Strategic planning framework for fisheries</td>
<td>2010 - 2019</td>
</tr>
</tbody>
</table>

Guided by the NSDP, the RGC has launched several clusters of sectoral strategies which is covering the period between 2006 and 2010, and is renewed to 2013 (MoP, 2010). Under each set of strategies are programs formulated by respective agencies that address SLM either directly or indirectly. Strategic policies and programs listed in Table 11 clearly show:
1. Land use planning and enforcement to regulate land use;
2. Enabling decentralized planning and decision making to promote SLM;
3. Ensuring large development projects are environmentally sound and SLM friendly;
4. Application of SLM approaches and technologies in production systems;
5. Providing enabling conditions such as land and resource access rights, women participation and similar enabling conditions, etc.
The strategies and programs cited in the table above a) promote decentralized and community-based natural resources management; b) introduce SLM technologies in production systems; c) support land tenure and resource access rights and the role of women. Most of the above programs are being implemented with support from donor partners.

The National Capacity Self Assessment done in 2006 (MAFF, 2010b) described the financing capacity for SLM as “severely lacking”. The more recent technical studies conducted to assess the nature and extents of land degradation particularly in agricultural landscapes imply that the gap between needs and resources could be widening. Financing for SLM is relatively young compared to financing for mainstream agricultural development programs. Nonetheless the relatively small financing that has been made available has generated several laudable technical and institutional innovations and best practices. While mainstream sources of development assistance trends have tended to decline in recent years due to the global financial crisis, new sources for financing has emerged. Preparatory work is undergoing to avail of opportunities for Reduced Emission from Deforestation and Degradation (REDD) while funding windows for climate change adaptation has increased (FA, 2009b).

2) Promoting SLM in agricultural lands
There are 4.37 million ha of agricultural lands that is the subject of the strategy for agriculture and water which has the following program components:

1. Support programs to build capacity for management of agricultural land and water resources;
2. Food security support program;
3. Agricultural and agri-business support program;
4. Water resources, irrigation and land management programs;
5. Agricultural and water resources research, education and extension programs.

Under ASDP, MAFF has prepared action plan to study and assess value of land resources and determine land suitability for different crops as well as to incorporate the introduction and application of new and appropriate technologies in order to increase productivity and address low soil fertility.

2.1) Agricultural land use planning
Agricultural land use planning can be done at the national and sub-national levels.

a) Agricultural land use planning at national level
On the national scale, agricultural zoning i.e. to designate and protect and develop areas for crop production has not been conducted. However, initial studies on land and soil capability for rice production have been done in selected provinces. Until 2010, Department of Agricultural Land Resources Management (DALRM) completed its 5-year strategic development plan for 2009-2013 and is now organizing its activities to deal with soil fertility management and improvement, land resources assessment and soil classifications.

b) Agricultural Land Law
There has been a lack of legislative developments in the area of agricultural land management and indeed, when compared with legislations on forests and fisheries, on the creation of appropriate arrangements for the development of policies and plans on sustainable agriculture.

Ministry of Agriculture, Forestry and Fisheries has included in its policy agenda for 2011 to 2015 the enactment of an agricultural land law to protect, conserve, and enhance the use of agricultural lands for productivity improvement and sustainability. MAFF have been in processes of preparation an Agricultural Land Law (ALL). This law is needed to provide the technical Department (DALRM) with the necessary powers to assist in the transformation of agriculture in Cambodia which is a fundamental element of the policies of the Government of Cambodia to bring about.

This law defines the framework for the management, use, and development of agriculture and land used for agriculture in the Kingdom of Cambodia. This law applies to all agricultural land whether public and/or private state lands, privately or communally owned lands in all agro-ecological zones in the country. The purpose of this law is to:

1. Ensure the sustainable management of agricultural land;
2. Bring about the increased productivity of agricultural land and the social and economic benefits that will flow from that;  
3. Ensure the protection of the environment including the conservation of the biological diversity and agricultural heritage of the Kingdom of Cambodia; improve soil and land conservation.

c) Agricultural land use planning at the local level
Considering that the agro-ecosystems analysis (AEA) tool can help farmers use land for agricultural production better from 2001 to 2009, the Department of Agricultural Extension (DAE) with the support of Cambodian Agricultural Extension Project (CAAEP) funded by AusAID implemented the agro-ecology analysis for 522 communes of 66 districts and 12 provinces. Technical recommendations and lessons have been compiled and disseminated to the stakeholders and farmers in the communes.

2.2) Research and extension on SLM technologies for agricultural lands
a) Technologies
MAFF has identified several technologies that need to be disseminated to farmers to conserve land, improve fertility and thereby improve and sustain the productivity. Most of these focus on the needs of lowland agricultural areas.

The combined use of chemical and organic fertilizers have been defined as very good option since it contributes to the increase in crop yields and maintain soil fertility. However, due to the insufficiency of the fertilizers and knowledge on its usefulness, only a small number of farmers apply the technique in their crop cultivation.

Integrated farming systems that combine cereals with legumes, trees and aquaculture, as well as ecological agriculture approaches, are being piloted. Integrated pest management (IPM) has been extensively promoted among rice farmers. The system for rice intensification (SRI) has been adopted in many communities. Farmers who adopt SRI can save seeds, lower their production cost and get higher crop yields.

Soil conservation technologies in upland agriculture are generally known by extension personnel but they have limited opportunities to apply that knowledge in the field. The concept of conservation agriculture (including minimum tillage methods) is being piloted in a few areas in Battambang and Kampong Cham. The function of agroforestry as a land rehabilitation and climate change adaptation measure is not yet well known. The FA with donor support, has started several pilots on agroforestry.

b) Research
Guided by the ASDP-MAFF (2010a), the current research priorities focus on the increase in quantity and effectiveness of appropriate technologies, in order to improve food security, food safety and sustainability in using natural resources. Cambodian Agricultural Research and Development Institute (CARDI) and DALRM are the institutions that play the most important roles in the research on agricultural land resources. NGOs working in sustainable agriculture also contribute to the effort through various action researches on ecological agriculture techniques.

The master plan for national agricultural research (MAFF, 2007) has laid down the following strategies that are related to SLM:

1. Improving the efficiency and effectiveness of technology development and transfer through more participation of the stakeholders in all stages of the research and dissemination processes. Moreover, the increase in resources for research and stronger linkages with other research institutions have also been strengthened;
2. Broadening the funding base and promoting participation of the private sector in the funding and provision of agricultural research and other related services;
3. Incorporating social, gender and environmental equity into the research, development and transfer of technologies;
4. Increasing and mainstreaming knowledge based on the adaptive research through interactions with international institutions, in order to get important data and research information;
5. Strengthening the capacity in implementing these strategies sustainably, especially to attract development assistance, retain quality staff and decentralize activities in agricultural services throughout the country.

c) Extension systems
To disseminate agricultural technologies, farmer-centered, extension methodologies have been developed and piloted. They have been observed to be successful. SLM technologies have been disseminated through the following systems:

1. Agro-Ecosystems Analysis (AEA) which is being used by the DAE to analyze land agro-ecosystems at commune level;
2. Technology Implementation Procedures (TIPS) which have been developed by CARDI, DAE and some other technical consultants, describe different techniques for improving agricultural sector in order to solve major problems of farmers;
3. Farmer field schools (FFS) which involve some major farmer based training activities, including training courses on different subject matters for farmers.

One special type of agricultural extension delivery system is extension work on irrigation management. Since less than 56% of irrigation facilities are in service (ADB, 2008), there is a need to develop community systems that enhance and sustain irrigation systems. An example of an innovation is the MoWRAM’s pilot work—the Participatory Irrigation and Water Management Approach (PIMD), being implemented with ADB support. Under this scheme, Farmer Water Use Communities (FWUC) co-manage small scale irrigation facilities. Results have been mixed (positive and negative) but the concept, when further improved, could be an additional way for involving farmer–stakeholders in the planning and implementation of sustainable land management practices.

2.3) National programs to adapt agriculture to climate change
RGC and a number of international organizations that work in Southeast Asia have shown their concern on the effects of climate change and contributed in the preparation of NAPA by highlighting 39 adaptation activities. Within the 38 projects, there are 20 prioritized activities that focus on different sectors, including coastal areas, water resources and agriculture. As a first step, the program has focused on the management of natural disasters such as floods and droughts.

MAFF with UNDP support is piloting specific measures for adaptation in the agriculture sector. One of these pilots is the project entitled: “Promoting Climate Resilience Water Management and Agricultural Practice in Rural Cambodia” which is implemented in Preah Vihear and Kratie. Key activities address water-related problems in the target areas. A more recent and larger initiative is the Cambodian Climate Change Alliance (CCCA) with multi-donor support. The CCCA is involved in capacity building, awareness building and provision of small grants to support local innovative local actions by communities, NGOs as well as government agencies.

2.4) Key concerns in current programs that address land degradation in agricultural lands
Generally, the information and knowledge on land degradation are limited at the national and local levels and this issue has not been considered or recognized as the major problem yet. For instance, agricultural production on the watersheds located in south-western, north-western, north-eastern and eastern parts of the country, which has caused lots of soil erosion problems, have not been solved and informed yet.

Cambodia's vulnerability to soil erosion is increasing and raising the potential for negative impacts on agriculture and the natural environment. Therefore, assessment of the scope of the issue needs to be conducted. At present, there is no compiled data on the erosion available. There is also a lack of data on land resource in upland areas. There has been very little research on understanding soil and measures to assure sustainable use of land.

The current agricultural extension has not included major priorities and goals of land conservation and improvement. The concept of agroforestry, which is a very good strategy not only for SLM but also for climate change adaptation, has not been studied in detail.

Due to lack of resources and manpower capacity, there is no clear program to provide technical guidance on SLM to large scale agribusiness ventures such as ELCs. Thus, proactive
technical guidance to ELCs operators to integrate SLM in business operations has not been adequate. Compliance to proper agricultural land use practices by ELCs also needs to be better monitored.

Application of the regulations and enforcements related to fertilizer and pesticide management and use is still limited. At present, RGC puts lots of efforts to develop laws and regulations on these inputs with the expectation that they will be approved or enforced in the near future.

The MAFF reorganization process is in the right direction, but the limited resources and capacity of its technical institutions related to agricultural land management is still the major challenge for the institutions to perform well.

3) Promoting sustainable management of forest lands
The technical working group (TWG) on forestry and environment has provided the overarching framework of interventions. Forest law and the recent launching of National Forest Programs (NFP) have provided further guidance on the management of forests, under the jurisdiction of the FA. Law on natural protected areas has also provided as the guidance for protecting natural protected areas in Cambodia. Through these two bodies, RGC has started the conservation of forest cover on the watersheds that are important in supplying water for agriculture and other sectors (FA, 2009a).

3.1) Managing forest cover in protected and production forests
a) Overall progress
A significant progress made by the TWG on forestry and environment was the completion of NFP which has identified six sub-programs to be implemented by FA from 2010 to 2029. On the other hand, the process of forest concession which has not been well managed has been converted to forest conservation system.

b) Protected forests
Protected forests have been managed for biodiversity conservation, environmental services and cultural values. They are also the sources of non timber forest products (NTFPs) for local people. So far, forest of 1,490,000 ha, which equals to 13.7% of the total forest land, has been defined as protected forests (FA, 2009a).

c) Management of watersheds
(1) Reforestation efforts
In addition to forest protection efforts, the FA maintains a tree planting program aimed at a) rehabilitation of degraded secondary forests; b) supporting community forestry; and c) large-scale plantations. There are three sources of action from government agencies (including the military), community forestry holders, and companies. The progress, which has been made by small-scale tree planting efforts, has been relatively slow. Reforestation activities are approximately 1,000 ha year⁻¹. The current tree planting program, supported by the NFP, espouses the promotion of indigenous species. It encourages mixed plantations and specifies conditions where monoculture plantations are appropriate or not.

(2) Management of flooded forests
Flooded forests benefit agriculture in the long term by helping regulate sedimentation and indirectly minimizing the intensity of floods. They support inland fishery productivity which in turn supports farm household income. The RGC has earmarked major portions of inland fisheries (including flooded forests) for community fisheries (CFi) management. Five hundred nine (509) CFIs have been established of which 179 have been registered. Government–community partnerships through CFi has brought about early positive impact on fishery productivity and improved institutional collaboration.

d) Management of forest and economic land concessions
Forest concession, a management system that allows large-scale harvest of forest products for the state revenue without deteriorating the forest resources, was introduced and enforced from 1994 to 1998. Since 2006 RGC granted the concessions for 6,498,088 ha or 60.73% of the total forest covers land to 29 private companies. However, due to the failures in following the contracts, land area of 3,501,170 ha was confiscated from 17 of the companies and defined as government property (FA, 2010). On 30
June 2006, RGC established secretariat for ELCs technical assistance to review and assess conditions before allowing contract preparation and to monitor and evaluate ELCs activities from time to time. Based on the data of MAFF and MoE, by 2010, ELCs cover approximately 1.6 million ha.

e) Role of community forestry (CF)
Community forestry is a form of forest management that empowers local communities to manage forest resources in a sustainable way. In December 2003, sub-decree on community forestry was approved by the government in order to officially recognize the roles and rights of the communities in accessing and utilizing forestry resources in a sustainable way (FA, 2009b). By 2010, 430 community forestry areas had been established to cover forestland of approximately 380,972 ha in 194 communes of 80 districts and 20 provinces. Some innovative pilot projects are being implemented with the communities’ forestry such as REDD in Odor Meanche and Mondulkiri provinces which aim at encouraging peoples to conserve forests.

3.2) Managing land degradation in natural protected areas

a) History of planning and overall progress
Natural protected areas are parts of land or sea dedicated to the protection and maintenance of biological diversity and relevant cultural resources, which are managed through legal or other effective means. The first protected area in Cambodia was Angkor Archaeological Park declared in 1925. The park covered 10,800 ha and was defined as the first for Southeast Asia at that time. At present, there are 23 natural protected areas (CPAs) in Cambodia which can be classified into four main types (national parks, wildlife sanctuaries, protected landscapes and multiple use areas) that cover over 3,402,200 ha of land. These areas have been established in November 1993 by a Royal Decree.

b) Community protected areas
The law on natural protected areas defines and categorizes the areas into four systems: 1) core zone; 2) conservation area/zone; 3) multiple-use area; and 4) community area. Based on the law, establishment of CPA is a system that allows communities to participate in the protection and use of natural resources in that defined areas in a sustainable way. By December 2009, 84 CPAs had been established to cover a total area of 93,339 ha.

3.3) Key constraints in addressing land degradation in forest and natural protected areas
Cambodia still lacks clear information on economic efficiency of different types of land use, which is the basis for decision-making on land use and forest land allocation. Moreover, budget for implementation of CPA plan, both at the national and grassroots level, is enough to ensure effective and sustainable management.

Implementation of the community forestry program has been constrained by the slow pace of legal recognition of community forestry applications. This has been partly attributed to conflicting land claims. The MAFF–FA is now fast tracking the identification of potential community forestry areas so that community forestry applications can be processed more expeditiously. This also provides early notice on what areas can be allocated to either economic land concessions or CF.

Some of the forest lands allocated to communities for their management have generally been of low quality. Thus, there may be insufficient incentive to protect forests in some areas. Meanwhile, the MAFF in collaboration with NGOS such as the Cambodia Working Group for NTFPs has stepped up efforts to enhance value addition of limited quantities of NTFPs from these forests.

In the case of Community Forestry, the registration of CF agreements needs to be accelerated to spread the positive impact to larger areas.

The current network of protected areas does not fully reflect the geographical distribution of biodiversity, thus, needs to be addressed. Financial and manpower limitations prevent both facilitating groups and CPA holders to expand the initial success of pilot work to wider areas.

The roles of local authorities as partners in forest protection have not been fully tapped. Unclear guidelines on their roles and lack of participation in the allocation of forest lands to various land seem to prevent communes from investing more funds to support CF. The MAFF-FA are presently piloting a “Partnership Forestry” approach which could provide the incentives to local governments to invest in local forest protection.
4) SLM for agricultural and forest landscapes (multiple landscapes)

4.1) Overall situation

The sections above described SLM interventions initiated by mainstream programs in agricultural lands (extension and research programs) and forest lands (CF and Reforestation; Protected Areas and CPA etc). The following sections describe the programs that cover both forest and agricultural lands. These include multi-sectoral efforts for watershed management; commune land use planning; and EIA processes.

4.2) Multi-sectoral efforts to protect watersheds

The RGC has adopted the river basin approach to protect the Tonle Sap Lake. The Tonle Sap Lake Authority fulfills the role of a river basin organization (RBO). MAFF with support of donor partners such as GTZ is also piloting the concept of watershed management approach to land management (particularly at the sub basin, watershed and sub-watershed levels).

This approach relies on multi-sectoral coordination in which the provincial government plays a crucial role. The current pilot project in Stung Siem Reap watershed is a good example of watershed management that harmonizes all national and local efforts and maximizes limited resources for addressing carefully set targets. Examples of targets set within the watershed framework are the provincial government’s regulation of sand mining.

A somewhat similar approach is being conducted in four sub-watersheds that contribute to the Mekong River and are shared by Kratie and Mondulkiri provinces. The MRC, in collaboration with the Cambodia National Mekong Committee (CNMC) and MAFF has developed several guides and training manuals on local watershed planning and management for MRC member countries.

Anecdotal information from localities indicates that there is increasing local appreciation on the role of lower level watersheds (micro watersheds) in agriculture. In one community forestry site, the community led in the protection and regeneration of natural forests in the watershed in order to arrest the deposition of sand into their lowland rice paddies (FA, 2010).

Localized watershed planning holds promise as a socio-technical strategy. Proven watershed planning tools can bring stakeholders together to harness both natural and man-made systems to better manage the risks of floods or droughts.

The approach has been proven in many parts of Asia (India, Vietnam, Philippines, etc). However, its adoption in Cambodia is hindered by lack of appreciation of its benefits. This is possibly because of a misconception that watershed management is solely the task of foresters. In reality, watershed management is much more than just forest protection. It also involves improving agricultural practices and protecting lakes and rivers in the downstream portions. It needs the contributions of all types of stakeholder such as forest dependent communities, farmers, urban water users to name a few.

4.3) Solutions to land degradation problems through land use planning process at commune level

The RGC established a council for land policy that is in charge of general land use planning and management in the country. Strategic framework for land policy highlighted decentralization in the land use management and planning as well as coordination processes for common use of land with natural resource management, under legislative and frameworks.

Planning for land use at commune level is a very good means to guide effective and sustainable land use in rural areas that are dependent on agricultural productivity. The RGC has piloted the concept of comprehensive land use planning (CLUP) at the commune level. National guidelines and training manuals have been developed. The Ministry of Land Management, Urban Planning and Construction (MLMUPC) aimed to initially help 120 communes complete their CLUPs.

Land use planning protocols include the protection of ecologically fragile landscapes. Communes believe that the CLUP process has enabled them to determine the long term land use needs of their communities. In areas where they have been piloted, CLUPS are used to guide the development of Commune Investment Plans (CIPS). The CLUP process needs the agreement of line agencies that ultimately make decisions on land allocation. A joint Prakas (declaration) is being worked out between the Ministries to improve inter-agency and line agency-local authority collaboration in the CLUP process.
4.4) Addressing land degradation through EIA system

The EIA process that has been officially implemented since March 2000 is a key technical framework for assessing environmental impacts in the preparation of master plan as a basis in the preparation of action plans, implementations and managements of development projects. EIA is a potentially powerful tool to ensure that ELC applications are environmentally sound and can help avoid potential conflicts between concessionaires and communities. However, implementing regulations for EIA on ELCs are not yet adequate or have not been consistently enforced. Thus, their value as a preventive and regulatory tool against land degradation has not been fully realized. The MOE is presently addressing this issue.

5) Best practices in SLM

5.1) Importance of best practices

UNCCD defined best practices as “measures, methods or activities that perform well or achieve highest results, in accordance with a set of criteria” Regions with best SLM practices are called “model places or places with best practices”. In that context, model places can be the ones that used to have land degradation problems, but the problems are being solved with substantive success. The best practices are important in providing concepts for the development of NAP or inform other regions that have had similar problems.

5.2) Documentation of best practices initiated by MAFF

At the end of 2010, MAFF with the support of SLM project, disseminated research findings on models of SLM best practices in Cambodia (MAFF, 2010b). The models include SLM in agriculture, as well as the conduct of community forestry, community fisheries and community natural protected areas. Best practices in SLM by local authorities were also documented. Detailed information related to the issue is described in the reports of the studies.

Examples of best practices for agriculture include SLM "approaches" that:
1. understand/improve the ability of government NGO extension personnel and community leaders to the agro-ecological situation of local communities as basis for commune level agricultural planning (e.g.: AEA);
2. Identify and understand the types of soils (e.g.: Soils Technology Information Package).
3. Facilitate land ownership to encourage long term farm investments;
4. Lower the cost of extension by involving farmers teaching other farmers
5. Improve the role of women;
6. Improve marketing for products from integrated farming (e.g. Siem Reap project).

Agricultural best practices also include a range of SLM friendly "technologies" such as:
1. Multipurpose farming to improve and stabilize farming systems.
2. Systems for rice intensification to improve rice productivity.
3. Composting to improve soil fertility management and soil and water conservation.

5.3) Lessons from the best practices

There is a common experience among communities with best practices. For example, transparent and participatory processes encourage communities to invest time and resources for SLM. Successful SLM is associated with government personnel who transformed themselves from regulators into facilitators. Community level knowledge sharing helps spread good practices. Communities who can engage with local authorities are usually more successful. Also, provincial governments play a crucial role in the resolution of competing land use priorities.

If the enabling environment would be provided, more communities, communes as well as field offices of government units would be able to adapt these best practices in their own situations. By doing so, good SLM technologies and approaches can be promoted in wide areas (in most communes) and at lower costs to government.
6) Capacity building for SLM and NAP

6.1) Obligations under UNCCD

The RGC is obliged to comply with UNCCD to develop human and institutional capacities. The national capacity self assessment (NCSA) for implementation of UNCBD, UNFCC, and UNCCD found that Cambodia still lacks human and institutional capacities as well as financial support. Moreover, stakeholders such as NGOs and private sector have the perception that their capacity is still limited, which means lower than the one of the RGC officers.

With the help of the NCSA, the government and non-government’s manpower who are dealing with programs on land degradation or SLM conducted a self assessment of themselves (MOE, 2005). Some of the key results include:

1. They are perceived to be "lacking" to "severely lacking" in the human, institutional, supportive and financial capacity. Capacity for UNCCD is the least problematic among the capacities for the three Multilateral Environmental Agreements or MEAS (CCC, CBD and CCD);
2. The capacity for financial support is lowest while human capacity was the highest;
3. NGOs and private sectors feel less "inadequate" about their capacities than government staff.

6.2) Assessment of stakeholders’ knowledge made by SLM project

Two assessments made in 2009 found that, in general, the government officers who were involved with the project had medium knowledge on types of causes for land degradation and best practices for SLM. At the same time, the capacity for policy analysis and resource mobilization were found limited. In MAFF, some departments raised some specific needs related to SLM, such as:

1. Department of Agricultural Land Resources Management (DALRM), which was very recently established, is now facing with a major challenge of most staff with very little educational background and experience on soil conservation and classification as well as agroforestry. These staffs need to be supported urgently with their capacity building;
2. Local agricultural extension workers have very limited knowledge on land or soil fertility management and they perceive the need to be equipped with technical skills so that they will be more able to help farmers improve soil fertility and conservation, etc.;
3. Department of Agricultural extension (DAE) also needs to strengthen its capacity for AEA, so as to have sufficient capacity to identify problems at the grassroots level related to SLM;
4. The Community Forestry Office of FA is concerned about the lack of current stock of NTFPs which are the basis for peoples’ livelihood activities. The office is interested in developing its capacity in promoting agroforestry to be the strategy for better management of small agricultural lands in the forest area;
5. Like the above-mentioned office, the Department of Research and Community Natural Protected Areas of MoE, which is in charge of the management of natural protected areas, is also concerned about the limited current stock of NTFPs and the role of agroforestry, that can contribute to maintain the products effectively;
6. The gender mainstreaming group of MAFF that is in charge of promoting women roles in agriculture and SLM has formed an appropriate mechanism in some specific locations. The group is concerned about the necessity in updating the existing guidelines for extension campaign to promote women role in SLM; and
7. Provincial and district facilitators responsible for the planning process that focuses on SLM at the commune level raised the necessity in learning the knowledge on different practical concepts and implementations for SLM.

6.3) NAP Contribution to systematic capacity building for implementation of UNCCD

The development of NAP is an effort to improve capacity systematically. The program is relevant to the agenda for policy reform as well as investment programs for facilitation and encouragement to stimulate multi-stakeholders’ support to SLM.

Capacity building for the institutions and human resource is a section that needs to be included in the capacity building programs of line ministries and development partners. SLM project analysed the problems and consequences of land degradation as well as prepared soil map using information on locations with the problems and locations with the models of best practices. Training activities on
SLM was prepared and organized for some technical officers. Documents on best practices relevant to SLM were identified, compiled and disseminated for wide adoption. Building the capacity in sustainable forest management is being practiced in accordance with the existing plans described in the NFP. For that, the Institute for Forest and Wildlife Research of FA was established and tasked to respond to the issue. Building the capacity of local authorities on SLM was undertaken in accordance with policy reform and RGC programs for decentralization and deconcentration supported mainly by DANIDA/DFID/NZ Aid. There are some more projects implemented by Ministry of Interior (MoI) with the objectives to build capacity of Commune councils. Many NGOs are complementing the RGC’s efforts to improve the capacity at the grassroots level for the management of agriculture, community forestry, community fisheries and community protected areas.

7) National action plan to combat land degradation and sustainable land management programs
This section discusses the overall scope of the NAP CLD in terms of target locations and practices and key stakeholders as well as the overall investment projects, phasing and lead actors. This also discusses the phasing of investments and the proposed coordination and management of the NAP.

7.1) Target Locations and Practices
NAP would be implemented in key agricultural landscapes experiencing various forms of land degradation. Table 11 discusses the targeted landscapes and the extent of the problem; the practices to be promoted within them; and the actual physical targets to be achieved. In each of the geographic areas and through networks of pilot sites, the program would promote SLM practices. These pilots would serve as future models for addressing land degradation problems on a much wider scale.

Strategic Objectives (SO), SO1 (On farm land and soil management) and SO2 (Restore watersheds) are relevant to the concerned goal. SO3 (Policy), SO4 (Human resources) and SO5 (Financing) are not involved directly in physical development activities. Activities related to SO1 will be spread throughout the country, especially for the locations that the practices are needed the most. Activities related to SO2, on the other hand, will be implemented within 10 watersheds. All of these have been considered to achieve good results from smooth management of agricultural land since the beginning.

Fig. 5. Key stakeholders in NAP CLD
7.2) Stakeholders

NAP is a multi-sectoral effort. Based on the stakeholder analysis in the previous section, the program will work with three types of stakeholders (Figs. 5, 6).

1st – The day-to-day land users such as farmers, agribusiness operators, CF etc. These include both upstream and downstream users of land and water resources.

2nd – Local catalysts such as local governments, field offices of line agencies and relevant civil society.

3rd – National Actors such as policy makers and development partners who provide with policy support at the national level.

Actual and direct on-farm investments are made by the first set of stakeholders. Landscape level actions are also made by the 1st set of stakeholders but in cooperation with the government. These on-farm and landscape level actions are in turn made possible by the combination of policy-based incentives; better planning and better delivery of support services that can be provided by the 2nd and 3rd level of stakeholders. Examples of policy based incentives and disincentives are better tenure security; and enforcement of agribusiness regulations etc. Harmonized local planning is exemplified by the watershed planning approach. Improved delivery of support services are exemplified by more effective extension services, more effective fertilizer recommendations, and better access to quality planting materials, etc.

Overall, NAP CLD consists of 5 Programs, 10 Sub-Programs and 30 Projects as listed in Table 12. These prioritized activities need to be funded and urgently implemented.
Table 12. Summary of programs, sub-programs and projects

<table>
<thead>
<tr>
<th>Strategic objectives</th>
<th>Programs</th>
<th>Sub-program</th>
<th>Projects</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO1: Land management and adaptation to climate change</td>
<td>1</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>SO2: Watershed and Forests</td>
<td>1</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>SO3: Policy Support</td>
<td>1</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>SO4: Human Resources</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>SO5: Financial Resources</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>5</strong></td>
<td><strong>10</strong></td>
<td><strong>30</strong></td>
</tr>
</tbody>
</table>

5. Conclusions and recommendations

We noted that there are a lot of issues and challenges arisen at all categorized land uses, in general, for both the lowlands and uplands of Cambodia. In order to help increasing productivity of the lowland and upland, and generating more incomes to farmers.

For the lowland, we need to update or extend the current soil classification system (Cambodian Agronomic Soil Classification, White et al., 1997) for a country-wise in terms of extra groups, phases, scale, volume and significance of use for crop production. Improvement of soil fertility is needed as most soils are low fertility in nature, and they are subject to use under rainfed conditions with significant fluctuations in nutrient and water availability. Crops’ yield remains relatively low in this condition, therefore, there is still large yield gain of crops to be made through adoption of fertilizer recommendations with site specific conditions and soil types, especially when good quality seed is used. We need to gain more productivity from the land/soil usage by promoting the intensification and diversification in the lowland cropping systems.

In the upland, there are no simple guidelines to classify, identify and manage upland soils. This is a major hindrance to the land utilization, and sustainable management upland soils. Very little has been done on land suitability. This is required to develop agro-ecological zoning in order to facilitate agricultural land-use planning and management in the country. Lack of comprehensive database of upland soil resources of the country, there is very little research has been carried out to understand the soils and overcome their constraints in order to allow for sustainable production. This is a major hindrance to sustainable management and increasing productivity of upland soils.

Although there were limitation of scopes and timeframe for study on LD in Cambodia, the sites selected in the study were becoming helpful to identify the nature of LD, the extent of LD, the hot and bright spots. Generally it can concluded that land degradation has been happening everywhere in Cambodia and there were still limited understanding among relevant stakeholders. Farmers recognized their crops’ yield decreased over times, and they tended to use more fertilizers to maintain the crop productivities without knowing the main causes of yield decline. Land degradations in the 5 selected studied sites were found with different nature of its degradation. Some forms of land degradation caused by human induced activities such as deforestation, mining, inappropriate agricultural practices, and some caused by its natural factor itself such as inherent low productivity soils combined with disaster risks and climate change induced such as drought, floods, etc.

The dearth of updated knowledge about land resources and its management, and lack of policy instruments have been ones of the major constraints on the productive and sustainable use of agricultural lands. The conversion of agricultural lands to other uses, and the unproductive use of lands are also the constraint facing the country’s land resources. In response to the current land uses and land degradation situation, the legal and institutional frameworks such as agricultural land law, and upgrading agricultural land administration, have to be soon finalised and effectively enforced, and the technical frameworks such as national action plan to combat land degradation and national strategy on
adaptation to climate change in agriculture that already identified some prioritized actions need to be urgently researched and implemented to better manage agricultural lands, forest, water and biological resources, as well as for better strengthening governance and financing aimed at providing benefits to the country and people.

Acknowledgement
We are grateful to the Royal Government of Cambodia and the United Nations Development Program in Cambodia, providing fund supports for this study. Both facilitation and technical assistance provided by the General Directorate of Agriculture and relevant Provincial Departments of Agriculture in the study areas are also gratefully acknowledged.

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