Investigation and evaluation of the risk of Cd contamination of agricultural land in typical areas

Yang Yu 1,2,3, Fusheng Wei3,4, Wenqing Liu1, Linlin Zhang3, Renji Xu3 and Guoping Wu3

1 Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230026, China; 2 University of Science and Technology of China, Hefei 230026, China; 3 China National Environmental Monitoring Center, Beijing 100012, China. 4 Email: weifsh@cae.cn

Abstract. The issue of food safety being compromised by heavy-metal contamination in soil has become the focus of increasing attention. Sampling points with a low, middle, and high Cd content in the soil were selected in Hunan Province. By sampling the soil and rice point by point, the total and the available Cd content and the content in rice were monitored. The 85 samples were subdivided into three groups according to the total Cd concentration: for the 25 low-risk samples, the content was 0.19–0.80 mg/kg; in the 51 moderate-risk samples, the content was 0.31–3.62 mg/kg; and in the nine high-risk samples, the content was 1.52–24.25 mg/kg. The results showed that: (1) the mean Cd concentration of the soil in the three groups was 0.45, 0.92 and 5.94 mg/kg, respectively; the available concentration was 0.30, 0.57 and 3.71 mg/kg; and the concentrations in rice were 0.09, 0.19, and 0.64 mg/kg. The total Cd content in the soil, the available content and the content in rice increase from low risk group to high risk group. (2) The Cd contents in rice show a significant positive correlation with the total amount in both the soil (the correlation coefficient (r)=0.343) and the available contents (r=0.377). (3) The total Cd content in the low-risk group is small, with three of the 25 rice samples exceeding the standard; the effective rate (available content/total content) of Cd was 50.7–97.5%. This showed that rice could still exceed the standard even when the total Cd content of the soil was low but the available content of Cd was relatively high. (4) Among the nine samples in the high-risk group, three did not exceed the standard; the effective rate of Cd was 32.7–62.5%, obviously lower than that in the rice samples that exceeded the standard (51.2–99.4%). This showed that even the total content was high and the available content was low, the Cd content in rice might not exceed the standard. (5) According to the total Cd content in the soil and the amount of Cd exceeding the standard in rice, the risk level was adjusted. After adjustment, the low-risk group contained 61 samples, the rate at which the standard was exceeded was 0%; the moderate-risk group had 12 samples, the excess rate was 75%; and 12 samples formed the high-risk group, where the excess rate was 100%. The adjusted classification is more consistent with what is expected from the standard grouping. The modification of the standard proposed here should improve the accuracy and thereby the usefulness of the standard, and may be useful for the improvement of similar laws and regulations in other countries.
1. Introduction

Heavy-metal pollution causes functional changes in the soil of agricultural land, affecting the quality of crops and endangering human health. Therefore, soil pollution is increasingly becoming the core of environmental pollution assessment and environmental governance. The land management policies, living habits, environmental conditions, and other aspects vary among different countries. The basic legislative framework for protecting the soil environment of agricultural land is slightly different [1, 2], which leads to great differences in the goals of protection and in the naming, use, kind, unit and other properties of data collected on the soil environment in different countries. Many countries set different thresholds to protect and control the soil according to the degree of soil pollution and risk. For example, Japan adopts a warning value and an action value, that is, beyond the action value; it must take repair measures or change the use of land to ensure the safety of land use. Similar measures are taken in countries such as Denmark, Switzerland, Austria, Finland, and South Korea [3].

The formulation of soil environmental quality standards is a complex problem. Heavy metals in the soil enter the human body mainly through the food chain. The heavy metals level of agricultural products in the food chain is critical. Therefore, in establishing an environmental quality standard for heavy metals in the soil of agricultural land, the contamination of agricultural products should be considered. In China, the prevention, control, and protection of soil contamination is still in the initial stage. For the evaluation of the environmental quality of soil, the total content of heavy metals has always been adopted [4], but evaluating the total content has some limitations. For example, at high background values, although the total content is high, the proportion that can be absorbed by plants may be small, and agricultural products will be little contaminated. If the total content is small and the activity of heavy metals is high, then the agricultural products may be considerably contaminated. Therefore, by only evaluating the total content of agricultural land it is difficult to objectively assess the potential risks; the availability and other aspects should be taken into consideration comprehensively.

On June 28, 2018, Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land (GB15618-2018)[5] was officially issued, which further refined the screening and control values for soil contamination and utilization of agricultural land. In the present study, some paddy soils and rice samples at various sampling points in Hunan Province were monitored, and a risk assessment was carried out according to this standard. Based on our analysis and discussion of the evaluation results, ideas are put forward for adjusting the standard in order to describe the pollution situation more accurately and thereby the usefulness of the standard, and may be useful for the improvement of similar laws and regulations in other countries.

2. Materials and methods

2.1. Sampling points

Referring to the Second soil survey (1978~1986) results of the Cd contamination level in Hunan Province, 85 plots were selected for sampling in areas with low, moderate, and high contamination. The 85 sampling points together with their coordinates are shown in Figure 1.

2.2. Sampling and preparation

2.2.1. Soil sampling. The sampling was carried out in more than 20 counties in the cities of Yangzhou, Changning, Changde, Yiyang, Changsha, Zhuzhou and Xiangtan Area in Hunan Province. All soils were drawn from the same upper horizon (0-20 cm). A 50 × 50 m sampling area was selected at each sample point. A total of 85 samples were collected.

All soil samples were spread out on a piece of kraft paper (80 × 110 cm) in an air-drying room, in a layer with a thickness of 2 cm. After removing plant leaves, crushed stone and so on, the samples were dried naturally. Following grinding and passing through a 100-mesh screen, they were analyzed for the total and the available Cd contents and pH.
2.2.2. Rice sampling. Rice plants were harvested from each soil sample position and were manually threshed to separate grains. Then, they were air dried to constant weights, and processed according to “The Testing Methods of Rice Qualities” published by Chinese Ministry of Agriculture (NY147-88) [6]. Hush from the rice grains was removed using a laboratory de-husker (OHYA-25, Japan). The brown rice was polished with a rice polishing machine (CPC 96-3, China) until the cortex was removed and the polished rice samples were ground to make powder in a ball mill (JXFM110, China).

2.3. Sample analysis

2.3.1. Analysis of the total Cd content in soil. For determination of total Cd in soil, portions of each 0.20 g of soil were digested with a mix of 5mL of HNO3+1mL of HClO4+1 mL of HF, and processed according to “Soil-quality-Determination of lead, cadmium-Graphite furnace atomic absorption spectrophotometry” (GB/T 17141-1997) [7]. The concentrations of Cd were determined using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent, 7700x) following a standard procedure.

2.3.2. Analysis of the available Cd content in soil. The air dried soil samples of 5g through 2mm pore size sieve are placed in a 100ml cone bottle. Add 25ml DTPA extractor with pipette. The suspensions were shaken for 2h(200rpm) at 25℃ and then centrifuged at 8000rpm for 10min and filtered through 0.45µm filter paper. The Cd concentration in filtrate was analyzed by ICP-MS(Agilent,7500a). All reagents used were of reagent grade.

2.3.3. Analysis of the Cd content in rice. For rice samples, 0.20g was digested with 7mL of HNO3. After cooling, resultant solutions were diluted to 50ml using ultra pure water to 50ml. The
concentrations of Cd in the filtrate were determined using ICP-MS (Agilent, 7500a) following a standard procedure.

2.4. Data analysis
SPSS software was used for one-tailed chi-square tests and correlation analyses. The least significant difference of the data was computed at a significance level of 95%.

2.5. Quality assurance and quality control
The same procedure without samples was used as control and three replications were conducted for each sample. Quality assurance and quality control (QA/QC) for Cd in soil and rice grain was estimated by determining Cd contents in the standard reference materials, soil GBW07405 (GSS-5, GSS-16 and GSS-28) and rice GBW(E)100377 respectively, approved by General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of China (AQSIQ), with a recovery rate in line with the requirements.

3. Results and discussion
As recommended by Standard GB15618-2018, the screening value and the control value of soil risk are determined taking the total Cd content of the soil into account; the threshold values varied by pH (Table 1). The 85 soil samples are divided into three groups according to their total Cd content. The first group comprised 25 samples; in this group, the soil risk is very low, with a total Cd content below the screening value. The second is the moderate-risk group, where soil had a certain risk (screening value < total content of heavy metal < control value); it contains 51 samples. The third group is the high-risk group, for which the soil risk is relatively high (total content > control value), and contains nine samples.

| Risk values (mg/kg) | pH ≦ 5.5 | 5.5 < pH ≦ 6.5 | 6.5 < pH ≦ 7.5 | pH > 7.5 |
|---------------------|----------|----------------|----------------|----------|
| Screening value     | 0.3      | 0.4            | 0.6            | 0.8      |
| Control value       | 1.5      | 2.0            | 3.0            | 4.0      |

3.1. Cd content in soil and rice
The total and available Cd content in the soil, and the Cd content in rice in the three groups is shown in Table 2. The available Cd content and Cd content in rice increase with increasing total Cd content in the soil.

| Group | N   | Total contents (mg/kg) | Available contents (mg/kg) | Contents in Rice (mg/kg) |
|-------|-----|------------------------|---------------------------|------------------------|
|       |     | Ave value | Min value | Max value | Ave value | Min value | Max value | Ave value | Min value | Max value |
|       |     |           |           |           |           |           |           |           |           |           |
| Group 1 | 25  | 0.45      | 0.19      | 0.80      | 0.30      | 0.09      | 0.51      | 0.09      | 0.01      | 0.44      |
| Group 2 | 51  | 0.92      | 0.31      | 3.62      | 0.57      | 0.09      | 2.45      | 0.19      | 0.01      | 1.98      |
| Group 3 | 9   | 5.94      | 1.52      | 24.25     | 3.71      | 0.85      | 12.42     | 0.64      | 0.05      | 1.67      |
| All groups | 85 | 1.31      | 0.19      | 24.25     | 0.82      | 0.09      | 12.42     | 0.21      | 0.01      | 1.98      |
The Cd content in rice is significantly positively correlated with the total and the available Cd content in the soil. The correlation coefficient between Cd content in rice and total soil content is 0.343, that between Cd content in rice and available content it is 0.377, and that between available and total content it is 0.954.

3.2. Variation of Cd Content in soil and rice with pH conditions
The pH affects the transformation of Cd into an available form in the soil and the absorption rate of rice to varying degrees. According to the standard requirements (GB15618-2018), the risk screening value and control value of Cd contamination in soil at different pH values are different. Therefore, each of the three groups was subdivided into four groups according to pH values (pH <5.5, 5.5–6.5, 6.5–7.5, and >7.5, respectively). The results of the survey are shown in Figures 2-4.

**Figure 2.** Cd content in low-risk rice at different pH values.

**Figure 3.** Cd content in moderate-risk rice at different pH values.
3.3. Risk judgment of safety of rice as food

According to the monitoring results, three samples in the low-risk group exceed the food safety standard by 0.20 mg/kg; an excess rate of 12.0%. In the moderate-risk group, 12 samples exceed the standard; the excess rate was 23.5%. Six samples in the high-risk group exceed the standard, i.e., an excess rate of 67.7% (Figure 5).

3.4. Suggestions for a comprehensive evaluation of Cd contamination

According to the description of three classes of soil in the standard (GB15618-2018), when the content of pollutants in the soil is lower than or equal to the screening value, the risk of soil contamination can be ignored; when the content of pollutants in the soil is higher than the screening value, but equal to or lower than the control value, there is a risk of excessive pollutants in edible agricultural products; and when the content of pollutants in the soil is higher than the control value, it is difficult to reduce the risk of edible agricultural products by agronomic regulation and replacement planting. There are some differences between the standard and the evaluation results in this study: (1) For the samples in the low-risk group, where the total Cd content in the soil is lower than the screening value, 12.0% of Cd in rice sample exceed the standard; (2) for the second group, where the total content is between the...
screening value and the control value, 23.5% of rice exceed the standard; (3) for the samples whose total Cd content is higher than the control value, 33.3% of the rice samples still do not exceed the standard.

The analysis shows that in the three samples exceeding the standard in the first group, the effective rate (available content/total content) of Cd is 50.7–97.5%, indicating that the rice still has the risk of exceeding the standard when the total Cd content in the soil is low and the effective rate of Cd is relatively high. In the second group, the total Cd content in six samples is two times higher than the limit (0.20 mg/kg), and the total soil concentration is 0.43–1.98 mg/kg; in the six other samples, however, the total Cd content is also higher, but less than two times. In the third group, the Cd levels in three samples do not exceed the standard; their effective rate is 32.7–62.5%, which is significantly lower than that of the other six samples in this group (51.2–99.4%), indicating that if, under conditions of a high total soil content, the effectiveness of Cd is low, the rice might still not exceed the standard.

Based on the above results, the standard risk in rice is exceeded more in the case of a large amount of the heavy metal in the soil, but if its effectiveness is low, the accumulation rate in the plant is also low and the rice may be risk-free. If the total content in the soil is low, but a large part is available, agricultural products still run the risk of exceeding the standard. We should pay attention to this, and monitoring and prevention should be improved. Although the total content is the source of Cd, this study shows that in some special cases, when classification is based on total content, exceptions still occur that do not conform to the characteristics of the group (i.e., When the content of heavy metals in soil was low, the content of heavy metals in rice exceeded the limit standard, which was inconsistent with the description of the low-risk group in the standard.). This shows that there are some limitations to grouping according to total content.

The total content, effectiveness, and absorption in rice of heavy metals should be fully considered and judged in studying the risk evaluation of soil contamination in agricultural land. At present, there is an evaluation standard for the total Cd content in soil in China; however, there is no corresponding evaluation standard for available content. The standard for rice in China is 0.20 mg/kg according to the "National Food Safety Standard of Maximum Levels of Contaminants in Foods (GB 2762-2012)". This standard is the same as that set by the European Union. In Japan and the International Codex Alimentarius Commission (CAC), where rice is the main staple food, the limit standard is 0.40 mg/kg[8].

In this study, the total Cd content in soil and the Cd content in rice (early rice) were suggested to be useful for comprehensive evaluation, and the risk level of soil pollution should be adjusted according to the degree to which rice exceeds the standard. A higher risk level was set when the Cd content in rice of the first group exceeded 0.20 mg/kg. When the Cd content in the second group was less than 0.20 mg/kg, the risk level was reduced by one grade; when the Cd content exceeded 0.40 mg/kg (twice the standard limit), the soil risk was increased by one grade; when the Cd content was 0.20–0.40 mg/kg, the risk level for the second group remained unchanged. When the Cd content of the third group was less than 0.20 mg/kg, the risk level was reduced. According to the above ideas, the samples were regrouped (Table 3). In the first group, the three samples of rice that exceeded the standard Cd content were adjusted to the second group. In the second group, 39 samples that did not exceed the standard were transferred to the first group; the excess levels of six samples were between 0.20 mg/kg (1×) and 0.40 mg/kg (2×), leaving this group unchanged; the six samples that exceeded the standard more than twice were moved to the third group. In the third group, there were three samples that did not exceed the standard; they were reclassified to the second group. After these adjustments, the first group had 61 samples, accounting for 71.8% of the total number of samples, and the excess rate was 0%. The second group had 12 samples (14.1%), with an excess rate of 75.0%. The third group had 12 samples (14.1%), with an excess rate of 100%. The overall conclusion was that this evaluation was more consistent with the grouping information described in the Standard (GB15618-2018).
Table 3. Results of risk group evaluation based on total amount of Cd in the soil and the content in rice.

| Preliminary classification of soil environmental quality | Category and description | Before adjustment | Adjusted |
|--------------------------------------------------------|--------------------------|-------------------|----------|
|                                                        |                          | Number | Percentage of total(%) | Excess rate(%) | Number | Percentage of total(%) | Excess rate(%) |
|                                                        | Low risk: Soil risk is very low, and causes little harm to the human body. | 25     | 29.4 | 12.0 | 61     | 71.8 | 0.0 |
| Group 1 (total value < the screening value)            | $R \geq 1$: raise one risk level and transfer to group two. |                    |           |            |        |        |        |
|                                                        | Moderate risk: There is some certain risk, but the soil will not cause much damage to the human body. | 51     | 60.0 | 23.5 | 12     | 14.1 | 75.0 |
| Group 2 (the screening value < total value < control value) | $R < 1$: Reduce one risk level and transfer to group one. 1 $< R \leq 2$: Leave in Group 2. $R > 2$, Increase level one risk and transfer up to group three. |        |        |        |        |        |        |
|                                                        | High risk: The soil risk is high and it is harmful to human health | 9      | 10.6 | 66.7 | 12     | 14.1 | 100.0 |

*R is a measure for the heavy-metal content in agricultural products, $R = \frac{(\text{Cd concentration})}{0.20 \text{ mg kg}^{-1}}$ in rice
4. Conclusions

(1) The total Cd content, available Cd content and the content of rice in the three groups increase from low risk group to high risk group. The Cd content in rice shows strong positive correlations with total content and available content in soil.

(2) There are some limitations to grouping the potential risks of agricultural soils based on their total Cd content. Rice growing at high Cd concentrations in the soil may not exceed the standard, whereas rice growing at low concentrations in the soil may exceed the standard. Therefore, the Cd content in both the soil and the rice should be taken into account.

(3) According to the total Cd content of soil and the degree to which Cd exceeds the standard in rice, the risk level of soil pollution is adjusted. After adjustment, the proportion of samples exceeding the standard rate is 0.0% in the first group, 75.0% in the second group, and 100.0% in the third group. The overall conclusion based on this evaluation is that the adjusted classification is more consistent with what is expected from the standard grouping. The modification of the standard proposed here should improve the accuracy and thereby the usefulness of the standard. It is hoped that the comprehensive evaluation results and ideas for adjustment presented in this study will optimize the evaluation methods, provide technical support for soil management and restoration. It can also be useful for the improvement of similar laws and regulations in other countries.

References

[1] Jeroen P, Christa C, Frank S 2006 Comparison of soil clean-upstandards for trace elements between countries: Why do they differ Journal of Soils and Sediments 6(3) 173-181

[2] Jeroen P, Lucas R, Frank S, Jan B, Claudio C, Marco D, Christa C 2008 Parameters causing variation between soil screening values and the effect of harmonization Journal of Soils and Sediments 8(5) 298-311

[3] XU Meng, YAN Zeng-guang, HE Meng-meng, ZHANG Chao-yan, HOU Hong, LI Fa-sheng, Human Health 2013 Risk-Based Environmental Criteria for Soil: A Comparative Study Between Countries and Implication for China Environmental Science 34(5) 1667-1678

[4] GB 15618-1995, Soil environmental quality standards [S]

[5] Nanjing Institute of Environmental Sciences, M, Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018), Ministry of Ecology and Environment of China: Beijing, China

[6] China, MoAotPsRo, Determination of rice quality, 1988, Ministry of Agriculture of the People's Republic of China: Beijing, China

[7] Center, CNEM, Soil-quality-Determination of lead, cadmium-Graphite furnace atomic absorption spectrophotometry, 1997, State Environmental Protection Administration: Beijing, China

[8] Guangdong stipulates that rice must have a cadmium report before it can be put on the shelves [EB/OL] [2013-05-22] http://news.sohu.com/20130522/n376697364.shtml