Contaminated Heavy Metals in Rice of Surin Province, Thailand

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Abstract

The purposes of this research were to investigate the types and quantities of contaminated heavy metals in rice, and to compare the heavy metals contaminated in jasmine rice, black rice and germinated brown rice in Surin province, Thailand, with the total of 15 rice samples. The experiment was performed using atomic absorption spectroscopy technique. The results showed that all rice samples had the amount of chromium in the range of 0.248–0.660 mg/kg. However, the detected amounts did not exceed the highest standard of chromium in cereal agricultural products according to the national standards of People’s Republic of China defined as 1.00 mg/kg. In addition, the amount of lead in the samples was not found, which the highest standard of lead given by European Communities and Food Standard Australia and New Zealand was defined as not more than 0.2 mg/kg. Therefore, all the rice samples used in this research were considered at safety level for consumption. This basic information is useful for consumers taking consideration to consume rice of Surin province safely.

Keywords: Jasmine rice, Black rice, Germinated brown rice, Heavy metal

Introduction

Rice is considered as an importantly economic stability and as an utmost economic plant in many countries, especially in most Asian countries (Phuong, Kokot, Chuong, & Tong Khiem, 1999) including Thailand. The economic importance of rice is very high, as seen from the increasing number of rice trading in the world market. More than half of the world has demanded to import rice; however, most rice–producing countries produce rice for their consumptions or probably import rice from foreign countries only unless the domestic rice production is enough.

Rice is a very important economic crop that brings a high proportional income to Thailand, creating an economic competition and power to purchase essential goods from abroad. Rice production in Thailand is an important sector of Thai economic development, with a large number of workers or farmers. Thailand has long tradition and culture of growing rice and has the fifth largest rice growing land in the world, which is the world’s number one rice exporter. The most cultivated rice in the country is jasmine rice. Most of the farmers in northeastern Thailand grow rice, Khao Dawk Mali 105, K15 and Khao Kiew 6 varieties (Kayee, 1999). Besides, a variety of rice landrace varieties are distributed throughout the region by choosing plant varieties according to the terrain for trade and according to the needs of consumers. Surin province, located in northeastern Thailand, has distinctive jasmine rice, which is the most popular rice in Thailand, creating a
reputation for Thailand as the number one rice of Thai people and a very importantly agricultural export product. The jasmine rice is not only delicious but also useful for health. Moreover, there are Hom–nin rice or black rice and germinated brown rice, which are the most popular rice varieties for Thai and foreign consumers. Because the black rice has different colors and long slender seeds, and there are many nutritional benefits such as 2 time–higher protein when compared to Hom Mali 105 rice, and also contains nutrients, especially the germ that is beneficial to health.

Generally, the process of rice cultivation requires the selection of areas that are suitable for planting and the understanding of the steps and factors of planting, such as disease control, pest eradication, fertilization rate and watering throughout the growth phase. At present, farmers are increasingly using pesticides and chemical fertilizers because it is labor saving and is convenient and increase productivity for farmers (Neeratanaphan et al., 2017). These reasons create a direct impact on consumers that heavy metals such as cadmium, lead, mercury, copper, chromium, iron, etc. are contaminated in soil and rice (Roya & Ali, 2017; Onsanit, Ke, Wang, Wang, & Wang, 2010; Jahed Khaniki & Zazoli, 2005) as found in some countries e.g. Iran and China. If the body receives a large amount of heavy metals, it causes health effects because they have many types that are defined in most food standards include lead and chromium (Food Standards Australia New Zealand, 2013). The dangers of these metals occur when the body exposes them. They will interfere with the work of the cell, being harmful to the cell wall, creating osteoporosis, destroying beneficial bacteria in the intestine, and inhibiting various enzyme systems causing the enzyme to work less and changing the structure of the biomolecules in the human body (Bundschuh et al., 2012; Ahmed et al., 2015; Jahed et al., 2005).

Due to the behavior of rice farmers, the improvement of rice varieties requiring high yield, resistance to the environment, rice pests and diseases, including the need to find better quality of rice varieties to meet the needs of the world market, they must use a higher amount of chemicals as well (Rice family Thailand, 2019). Besides, to our knowledge there have been no studies about contaminated heavy metals in rice of Surin province. Therefore, the researcher is aware of the impact on consumer health, if receiving heavy metal contaminants in excess of the standard criteria into the body, resulting in toxicity to health. Then, we studied the residual chromium and lead metals in rice samples in Surin province to provide inevitably basic information on the quality of rice and to examine the unknown and non–studied amount of heavy metals contaminated in rice as well as to realize the dangers that will be occurred.

**Methods and Materials**

This research was randomly collected the rice samples from January to February 2019, which were available in the market, supermarket and rice mills in Surin province, Thailand. The samples were classified into 3 types of rice, namely jasmine rice, black rice, and brown rice. Each type was experimented for 5 samples, totally 15 rice samples, for examining heavy metals using atomic absorption spectroscopy (AAS) technique.

**Sample preparation**

The 15 rice samples were ground with a mortar, and then weighed 1.0 g of fine–grained rice into the Erlenmeyer flask. The digesting sample was added with 10 mL of concentrated nitric acid and 1 mL of perchloric acid and left at room temperature for 24 h. After that, they were decomposed at 180 °C for 1 h to
complete the digestion, then filtered the solution into the 100 mL volume bottle and adjusted the volume by 2% nitric acid to the volume limit. The standard solution was prepared to compare with the sample solution. The digested solution was analyzed for Pb and Cr contents by flame and graphic furnace atomic absorption spectrometer HGA 900, PerkinElmer. Finally, the samples were analyzed to determine the amount of heavy metals with atomic absorption spectrophotometer.

**Standard solution preparation and % recovery**

The standard chromium solutions at concentrations of 0, 0.5, 1, 1.5 and 2 ppm were prepared. After that, the standard chromium solutions were pipetted to the desired concentration, then adjusted the volume with 2% nitric acid to 100 mL. The standard lead solution was prepared as same as the standard chromium solution. The % recovery of heavy metals in rice sample was measured by adding a standard solution to the sample solution and analyzing the amount of heavy metals with AAS technique.

**Results and discussion**

The results of the amount of chromium and lead in all 3 types of rice samples in the total of 15 samples with AAS technique found that all rice samples found chromium in the range of 0.248–0.660 mg/kg as shown in Table 1. They were considered to be in all standards when compared with the highest standard of chromium in cereal agricultural products according to the national standard of the People’s Republic of China, which determines the maximum value of 1.0 mg/kg (Ministry of Health of the People’s Republic China, 2013).

<table>
<thead>
<tr>
<th>Rice type</th>
<th>Sample Code</th>
<th>Chromium content (mg/kg) *</th>
<th>Lead content (mg/kg) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>J1</td>
<td>0.248 ± 0.034</td>
<td>0.200</td>
</tr>
<tr>
<td></td>
<td>J2</td>
<td>0.300 ± 0.024</td>
<td></td>
</tr>
<tr>
<td></td>
<td>J3</td>
<td>0.296 ± 0.033</td>
<td></td>
</tr>
<tr>
<td></td>
<td>J4</td>
<td>0.357 ± 0.031</td>
<td></td>
</tr>
<tr>
<td></td>
<td>J5</td>
<td>0.414 ± 0.011</td>
<td></td>
</tr>
<tr>
<td>Jasmine rice</td>
<td>B1</td>
<td>0.465 ± 0.040</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>0.446 ± 0.030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>0.496 ± 0.012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B4</td>
<td>0.514 ± 0.023</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B5</td>
<td>0.527 ± 0.033</td>
<td></td>
</tr>
<tr>
<td>Black rice</td>
<td>G1</td>
<td>0.571 ± 0.056</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G2</td>
<td>0.660 ± 0.041</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G3</td>
<td>0.607 ± 0.006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G4</td>
<td>0.596 ± 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G5</td>
<td>0.622 ± 0.020</td>
<td></td>
</tr>
<tr>
<td>Brown rice</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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* = the % recovery of heavy metals measured in the range of 80 – 110

* = the LOD of the instrument are 0.00078 for Cr and 0.0008 for Pb
When comparing the amount of chromium in all 15 rice samples, the samples of J1 fragrant rice had the lowest amount of chromium as 0.248 mg/kg, while the brown rice G2 had the highest chromium content of 0.660 mg/kg, respectively. The highest chromium content was found in the sample of G2 brown rice, which had a higher amount of chromium than other types of rice, as illustrated in Figure 1. This is probably due to the process of brown rice husking. On the other hand, the jasmine rice has rice color or rice scrub, removing the rice hull more, so it is possible that there is an erosion of heavy metals left in the grain. Therefore, the jasmine rice found less chromium content than other types of rice.

![Figure 1](image)

**Figure 1** Comparison of heavy metals, chromium and lead in rice samples

0.00* = Lower than Low Concentration (LLC) is lower than the lowest concentration in the range that can be found.

Results of the test for lead metal content showed that no amount of lead was found in all samples. This value is lower than the lowest concentration in the straight line, where the method can be found. It is considered in the range that does not exceed the total standard value, compared to the highest standard of lead given by European Communities and Food Standard Australia and New Zealand, which is defined as not more than 0.2 mg/kg (Official Journal of the European Union, 2014; FAO/WHO, 2009). Therefore, this information illustrates that the levels of lead metal are in the criteria that is very safe for consumption.

Moreover, when comparing the amounts of both heavy metals among all rice samples, the amount of chromium was higher than lead in all rice samples as shown in Figure 1. The reason is due to chromium being used as a factor in the production of equipment in various industries such as the tanning industry, textile industry and dyeing in the community. Additionally, it is found in wastewater caused by leaching of industrial plants, garage, petrol stations and other waste sources and sewage into water sources, etc. For agriculture, most farmers use water from natural sources for agriculture and then cause the accumulation of heavy metals in the soil. Therefore, there are contaminations of heavy metals in agricultural products.

When comparing the results with the research of Siri-anusornsak, Soiklom, and Thanaruksa (2017) who studied the amount of heavy metals, cadmium, chromium and lead in the Thai grains, it was found that 54
samples of rice samples were contaminated with heavy metals such as cadmium, chromium and lead. There were 15 white rice samples, 6 brown rice specimens and 2 black rice samples which found that the chromium contamination percentage exceeded the standard values in rice samples, which the white rice, brown rice and jasmine rice were 33.33%, 23.81% and 50.00%, respectively. In addition, the samples of white rice, brown rice and sapphire rice were contaminated with lead exceeding the standard value of 40.74%, 23.81% and 83.33%, respectively. Besides, it showed that the studied rice had heavy metal contamination exceeding the specified standard, especially chromium and lead that contaminated at an unacceptable level. This may be due to the different sources of rice samples and the length of time for collecting samples of rice used in the study, resulting in different amounts of heavy metals. Therefore, controlling the amount of heavy metal contaminated to the acceptable level is an important quality assurance of rice prior to export.

However, according to previous studies, aside from studying heavy metals such as chromium, lead and cadmium, arsenic is another metal that is high and often contaminated with rice, especially rice that needs to be exported for international trade. Meharg et al. (2008; 2009) analyzed the amount of arsenic contamination in Thai rice, in particular the standard arsenic analysis method, and the determination of inorganic arsenic values, which are more toxic than all arsenic. Particularly, inorganic arsenic is a dangerous substance and can cause cancer. They investigated the amount of arsenic in white rice (39 samples) and brown rice (45 samples) collected from many places including local markets and supermarkets, and the results showed that brown rice had higher inorganic arsenic content than white rice. The results also revealed that the analysis of arsenic content in polished white rice obtained from 10 countries (4 continents) including rice from Thailand as well. Additionally, rice samples from Egypt and India had the lowest total arsenic contents with 0.04 and 0.07 mg/kg, respectively and rice from the United States and France had the highest arsenic contents with 0.25 and 0.28 mg/kg respectively. The white rice from Thailand (54 samples) had a total arsenic content of 0.14 mg/kg in the range of 0.01–0.39 mg/kg) that arsenic detected in most rice is in the form of inorganic arsenic. In addition, Adomako, Williams, Deacon, and Meharg (2011) collected samples of rice, corn, wheat, and millet from markets in Africa, Europe, North America, South America and Asia (21 countries, 5 continents) to analyze arsenic content in rice. It was found that the rice from the United States had a higher total arsenic content (0.22 mg/kg), rice from Thailand (0.15 mg/kg) and rice from Ghana (0.11 mg/kg). Inorganic arsenic was found as high as 83% (42% for American rice and 67% for Thai rice) that the total arsenic content in other rice samples was only 0.01 mg/kg.

Furthermore, the rice samples used to determine the amount of chromium and lead in this research found very small contents and considered under the acceptable standards. This information indicates that the area used for rice cultivation and the producing process used in cultivation are in good conditions, allowing all types of rice produced with good quality and high safety in consumption. As a result, rice cultivated in Surin province is considered as an important rice-growing area which is famous for producing the top organic rice in Thailand. The identity of Surin province makes it possible to export jasmine rice and sapphire rice to both domestic and international markets because they are popular and accepted by plentiful consumers around the world. According to the rice samples used to determine the amount of chromium and lead in this research considered to the acceptable standards corresponding with the research of Nookabkaew, Rangkadilok, Mahidol, Promsuk, and Satayavivad (2013), the extraction and HPLC–ICP–MS analysis for arsenic speciation in rice were investigated. A simple extraction with water and digestion with amylase followed by the analysis using
ion-pairing mode HPLC separation was developed. A total of 185 rice samples (various types of rice) collected from different four regions in Thailand and some other Asian countries were analyzed. The total arsenic and inorganic arsenic in rice samples were in the ranges of 22.51–375.39 and 13.89–232.62 μg/kg, respectively. In addition, Cheun-im, Sinbuathong, Ingkapradit, Inklang, and Hom-ngarm (2009) studied on the concentrations of cadmium (Cd), chromium (Cr), lead (Pb), copper (Cu), nickel (Ni), zinc (Zn), and iron (Fe) in rice from organic paddy fields at Pathumthani Rice Research Center (PRRC) and Agricultural Service Center (ASC), Pathumthani Province. The results showed that there were no Cd, Pb and Ni in seeds. The other heavy metals that found in seed, stem and husk were much lower than the critical levels in plants. This indicated that the levels of heavy metals in the parts of seed, stem and husk were acceptable and those of seed were much lower contaminated than the stem and husk.

Moreover, heavy metals can be left in the environment and rice parts that Kingsawat and Roachananakanan (2011) investigated the concentrations of heavy metals in the water, soil, and rice in paddy fields, and compared heavy metal concentrations in the water, soil, and four parts of the rice plant (root, shoot, grain, and husk) between organic paddy fields and conventional paddy fields in Samut Songkhram Province, Thailand. The water, soil, and rice samples were prepared for heavy metal analysis using a microwave digestion system and heavy metal concentrations were determined using AAS technique. The results illustrated the accumulation of heavy metals in the water, paddy soil, and four parts of the rice plant as follows: Zn > Cu > Cd and the concentrations of heavy metals in samples were also found as follows (greatest first): paddy soil > rice root > rice shoot > rice grain > rice husk > water.

Recently, researchers, especially in the Asian region, have been alert to investigate for heavy metals contaminated with rice in order to stabilize international trade and consumer safety. For example, Mu et al. (2019) collected the rice plant samples from 19 provinces in four major rice producing areas of China to assess the geographical variation in total arsenic (As), Cd and Pb concentrations in the soil–rice system. Total average concentrations of As, Cd and Pb were consecutively 11.8, 0.45 and 25.7 mg kg⁻¹, and 0.089, 0.087 and 0.036 g kg⁻¹ in the polished rice. The national maximum allowable concentrations of total As and Cd were exceeded in 6.19 and 33.6% of soils and that of Cd was exceeded in 7.96% of polished rice and no polished rice exceed the Pb limit. The As, Cd and Pb concentrations of rice were significantly and positively correlated (p < 0.05) with their corresponding soil available concentrations rather than with their soil total concentrations. Chen, Tang, Wang, and Zhao (2018) studied a high risk of Cd exposure from rice consumption for the population of southern China. They collected 160 polished rice from local markets in 20 provinces in China and determined total Cd and As concentrations and As speciation. Total Cd concentration ranged from below the detection limit to 0.77 mg kg⁻¹, with 10% of the samples exceeding the Chinese limit (0.2 mg kg⁻¹). Rice Cd concentration showed a distinct geographical pattern, increasing from low levels in the north to high levels in the south of China. Median daily Cd intake from rice varied from 0.01 μg kg⁻¹ body weight in the north to 0.61 μg kg⁻¹ body weight in the south of China, representing between 1% and 73% of the tolerable daily intake (TDI) recommended by FAO/WHO. And, Xiao, Hu, Li, and Yang (2018). (2018) analyzed the spatial distribution of heavy metal monitoring data in paddy rice to provide a scientific basis for food safety risk assessment. In this study, the spatial distribution data of heavy metals (cadmium, lead, total arsenic, total chromium, and total mercury) in rice collected in the main production provinces of China were analyzed by multidimensional visualization and aggregation analysis.
Results showed that cadmium content in rice was higher than the limit value in some areas of Hunan, Sichuan, Guangxi and Anhui Provinces in China. With respect to other heavy metals, a small area of Sichuan Province experienced lead levels in rice higher than the limit value. Also, the arsenic level in rice was higher than the limit value in Jiangxi Province, a northern area of Liaoning Province and most parts of Guangzhou and its surrounding areas. In contrast, chromium was only detected at excessive levels in southern Sichuan Province. In addition, a small part of the eastern Sichuan Province was found to have excessive levels of arsenic. Moran’s I index of cadmium, arsenic, chromium, lead, and mercury in rice was 0.50, 0.55, 0.21, 0.09, and 0.05, respectively, which revealed a spatial autocorrelation.

Besides, Kwon, Nejad, and Jung (2017) collected the rice samples from four representative abandoned metal mining areas in Korea and analyzed for As and heavy metals, including Cd, Cu, Pb and Zn, by atomic absorption spectrometry (AAS). Average levels of As, Cd, Cu, Pb and Zn in agricultural soil samples were 64.4, 2.31, 63.5, 146 and 393 mg kg⁻¹, respectively. In addition, the average contents of As, Cd, Cu, Pb and Zn in rice grain grown on the contaminated soils evaluated were 0.247, 0.174, 4.69, 0.804 and 16.8 mg kg⁻¹ (dry weight, DW), respectively. These levels were relatively higher than worldwide averages reported by various researchers. Consequently, regular rice consumption grown in soils especially in the mining areas can cause health problems for local residents. Al–Saleh and Abduljabbar (2017) determined the levels of heavy metals in 37 brands of imported rice commonly consumed in Saudi Arabia after soaking and rinsing with water, and their potential health risks to residents were estimated by three indices: hazard quotient (HQ), hazard index (HI) and cancer risk (CR). The mean levels of lead, cadmium, methyl mercury and total arsenic in soaked (rinsed) rice grains were 0.034 (0.057), 0.015 (0.027), 0.004 (0.007) and 0. 202 (0. 183) µg/g dry weight, respectively. Soaking or rinsing rice grains with water decreased lead and cadmium levels in all brands to safe levels. All brands had total arsenic above the acceptable regulatory limits, irrespective of soaking or rinsing, and eight soaked and 12 rinsed brands contained methyl mercury. The levels of all heavy metals except cadmium were above the acceptable regulatory limits when the rice was neither rinsed nor soaked. Weekly intakes of lead, cadmium, methyl mercury and total arsenic from soaked (rinsed) grains were 0.638 (1.068), 0.279 (0.503), 0.271 (0.309) and 3.769 (3.407) µg/kg body weight (bw). The weekly intakes of lead and methyl mercury from the consumption of one rinsed and two soaked rice brands respectively, exceeded the Provisional Tolerance Weekly Intake set by the Food and Agriculture Organization and the World Health Organization. Fang et al. (2014) studied four common heavy metals: Pb, Cd, As and Hg in rice of China. Ninety two rice samples were collected from the main rice growing regions in China were collected from typical markets in Nanjing City. The results showed that Pb, Cd and As contents in rice samples were 4.3%, 3.3% and 2.2%, respectively, being above maximum allowable concentration (MAC). Therefore, more than 95% rice samples in our test had high edible safety.

Furthermore, not only did the researchers study the amount of heavy metals left in rice samples, but also other products made from rice were also studied for heavy metals contaminated with. For example, Londonio et al. (2019) studied the concentration of toxic and potentially toxic elements in rice samples, rice crackers, rice noodles, infant cereals and rice vinegar available in the Argentine market. The determination of nine elements, namely As, Cd, Cr, Hg, Ni, Pb, Sb, Se and Zn in 29 samples was performed using inductively coupled plasmamass spectrometry, which element concentrations spanned the ranges as follows: As (67–858
ng g⁻¹), Cd (<0.2–24.0 ng g⁻¹), Cr (36.6–937 ng g⁻¹), Hg (<50 ng g⁻¹), Ni (38.6–1040 ng g⁻¹), Pb (<2.0–139 ng g⁻¹), Sb (<3.0–24.7 ng g⁻¹), Se (<8.4–178 ng g⁻¹) and Zn (129–32400 ng g⁻¹). Mercury was not detected in any of the analyzed samples. The highest concentration (32.4 µg g⁻¹) was found for Zn in infant cereals according to the label added by the manufacturer. To assess accuracy, NIST 1568a rice flour was analyzed and results were in good agreement with certified values. Xie et al. (2017) assessed the cadmium (Cd) and lead (Pb) content in both white and whole meal flour milled from 110 leading rice cultivars. The white flour Cd content ranged from <0.0025 to 0.2530 mg/kg (geometric mean (GM) = 0.0150 mg/kg), while its Pb content ranged from <0.0250 to 0.3830 mg/kg (GM = 0.0210 mg/kg). The indica types took up higher amounts of Cd and Pb than did the japonica types. Although the heavy metal content of whole meal flour tended to be higher than that of white flour, nevertheless 84.5% (Cd) and 95.4% (Pb) of the entries were compliant with the national maximum allowable concentration of 0.2000 mg/kg of each contaminant.

**Conclusion and Suggestions**

All the rice samples collected from local markets and supermarkets in Surin province, Thailand, found very small amounts of chromium and lead and were in the highest standard in cereal agricultural products according to the national standards of the People's Republic of China, European Communities and Food Standard Australia and New Zealand, being considered safely for consumption. Therefore, this information can be preliminary utmost for consumers to choose in order to consume rice products of Surin province safely.

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