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Determination of Arsenic in Thai Rice

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Abstract

Studies have shown that rice (*Oryza sativa* L.) is one of the main sources of inorganic arsenic in foods. Rice absorbs arsenic from the soil and more so when planted in soils contaminated with agrochemicals residues. In this research, the concentration of arsenic in over 40 rice samples, selected randomly from paddy fields in the North of Thailand, was determined by inductively coupled plasma–mass spectrometry (ICP-MS). It was found that the average levels of arsenic in rice grown in uncontaminated soil was 1.8 $\times 10^{-3}$ mg kg^{-1} (1.8 ppb) relatively lower than the guideline of 0.2 mg kg^{-1} (200 ppb) agreed by Codex Alimentarius for arsenic in rice. Thus, it is possible to suggest that a normal intake of Thai rice from the paddy fields of North Thailand, would not pose any significant adverse health effect on the consumer and import restriction of such produce on the ground of safety will be unreasonable.

Keywords: Arsenic; Food contaminants; ICP-MS; Thai rice

Introduction

Arsenic is a toxic heavy metal that is widely distributed in the Earth's crust and found naturally in the environment. In humans, it is possible to be exposed to arsenic through air, soil, water and food. Rice (*Oryza sativa* L.) is the staple food and a source of energy and nutrients for more than half the world's population [1]. Nowadays, approximately over 90% of rice worldwide is grown in Asia, including Thailand, and it is estimated that annual rice production will increase from 524 million tonnes to 700 million tonnes by 2025 [2].

Thailand has been for several decades one of the world's largest rice producers and in some years, the world's number one rice exporter. The sale of rice for export has increased gradually from 4.0 million tonnes in 1990 to 10.6 million tonnes in 2011 [3]. By the end of 2016, Thailand exported around 8,712,050 million tonnes of rice worldwide [4]. In 2017, Thailand is expected to increase rice exports to 9.7 million tons [5].The quality of rice can directly impact on human health.

The determination of inorganic arsenic in rice has become very important during the last few years, since As (III) and As (V) are considered carcinogenic, and have been found at high concentrations in rice and rice products. Based on the analysis results by the U.S. Food and Drug Administration [6] rice (including Thai jasmine) and rice based products have been found to contain inorganic arsenic, sometimes at high levels. A study by [7] also reported that arsenic was found in Thai Jasmine rice at concentrations ranging between 0.04–0.40 mg kg^{-1}. Furthermore, many studies have indicated that a high concentration of arsenic often accumulate in rice grains [8-10]. In addition, arsenic has been found in rice and many rice products, for example, breakfast cereals, baby rice crackers and Japanese rice condiments. In fact, high content of 75.2-90.1% inorganic arsenic has been found in some rice products [11-13] raised a concern that rice would be the highest source of arsenic intake by humans except where countries have arsenic contamination via drinking water.

It has been reported that skin cancers can be related to arsenic intake, via drinking-water [14, 15]. Guo, 2004, reported that a level of arsenic exceeding 0.64 mg l^{-1} can cause lung cancer in humans. In addition, in West Bengal, arsenical skin lesions were found in people drinking tube-well water which contained arsenic concentrations above the World Health Organization (WHO) set limits (10 µg l^{-1}), and some areas had even higher levels than the national standard of 50 µg l^{-1} [16, 17] suggested that the number of fetal deaths was likely due to the drinking of tube-well water with a high arsenic concentration by pregnant women. A study by Davis et al., 2015 reported that high exposure to inorganic arsenic can adversely affect fetal development in pregnant women. In addition, Bangladeshi adults were affected by arsenic poisoning through the intake of large quantities of arsenic-contaminated rice and drinking water [18]. The accumulation of arsenic in rice can be increased due to the use of arsenic-contaminated irrigation water exceeding the permissible limit for drinking water (0.01 mg l^{-1}) stated by [19] (Food and Agriculture Organization of the United Nations) and WHO [20]. The [21] suggested that the maximum limits of inorganic arsenic at 150 ppb (0.15 mg l^{-1}) for rice grain and 75 ppb (0.075 mg l^{-1}) for rice products could reduce the risk of cancer in humans. In the European Union, acceptable limits have been introduced for inorganic arsenic in rice (0.20 mg kg^{-1}), rice products (0.30 mg kg^{-1}) and baby and toddler rice products (0.10 mg kg^{-1}) by the Commission Regulation [22] (EU) 2015/1006, amending Regulation (EC) No 1881/2006, setting maximum levels for certain contaminants in foodstuffs [17].

The aims of the present study were to determine the concentration of arsenic in 43 different Thai rice samples collected from the Phayao and Chiangrai provinces in the North of Thailand and to consider whether the concentrations were above the Codex Alimentarius' guideline value of of 0.2 mg kg^{-1} (200 ppb), [18].

Materials and Methods

Overview

Samples of Thai rice (n=43) were collected from different locations in Chiangrai and Phayao provinces, North of Thailand in the years 2014 and 2015. The rice plants were grown during the rainy season between June-July 2014, and were harvested in November 2015 (approximately 180 days after seed sowing). As far as can be ascertained, the rice plants were cultivated in uncontaminated arsenic paddy fields. Hydration was provided by rain water. The harvested rice samples were sun dried and stored in a cool dry place. The concentration of the arsenic was determined using inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS was chosen for it has high detection limit, selectivity, accuracy and precision [23-26]

Sample Preparation

43 rice samples were randomly selected and coded (Table 1). The samples were hand-milled with a mortar and pestle.

RF power: 1550 W
Auxilliary gas: 0.8 l/min
Nebulizer gas: 1.05 l/min
Sampler and skimmer cone: Ni
Mode: KED mode

Table 1: The ICP-MS operating parameters.

This process was performed to remove the husks from the rice seeds. The rice grains were then powdered using a domestic coffee grinder. The powdered rice samples were weighed accurately to a weight of 5.0 g into 100 ml volumetric flask to which 10 ml of 70% concentration nitric acid (HNO_3) was added. The rice samples were heated using a hot plate for 1 hour and then diluted with a standard solution which consisted of 3 litres of 2% HNO_3 + 0.5% HCl (hydrochloric acid) + 5ppb Rh (rhodium) + 200ppb Au (gold). The sample solution was diluted at a ratio of 1:10 by transferring 1 ml of the sample into a 10 ml volumetric flask. The 43 rice samples plus one blank were analyzed with a Thermo ICAP Q ICP-MS.

Chemicals and Reagents

2% HNO_3, 0.5% HCl, 5 ppb Rh, 200ppb Au was purchased from Fisher Scientific UK Ltd. Bishop Meadow road, Lough borough LE11 5RG. Pure water was collected from University of Reading.

ICP-MS analysis

Rice samples were analysed using a Thermo an ICAP Q ICP-MS (Thermo Fisher Scientific, UK) with a CETAC ASX-520 auto sampler. A PFA Micro Flow nebulizer attached to a glass cyclonic spray chamber was used for sample introduction. The ICP-MS operating parameters are listed below (Table 2) and the number of replicate is three.

Type of rice	Name of mutant rice	Code of rice samples
Glutinous rice	RD6	RD6-1
Glutinous rice	RD6	RD6-2
Glutinous rice	RD6	RD6-3
Glutinous rice	RD6	RD6-4
Glutinous rice	RD6	RD6-5
Glutinous rice	RD6	RD6-6
Glutinous rice	RD6	RD6-8
Glutinous rice	RD6	RD6-9
Glutinous rice	RD6	RD6-10
Glutinous rice	RD6	RD6-11
Glutinous rice	RD6	RD6-12
Glutinous rice	RD6	RD6-13
Glutinous rice	RD6	RD6-14
Glutinous rice	RD6	RD6-15
Glutinous rice	RD6	RD6-16
Glutinous rice	RD6	RD6-17
Glutinous rice	RD6	RD6-18
Glutinous rice	RD6	RD6-19
Glutinous rice	RD6	RD6-20
Plain rice	RD15	RD15-1
Plain rice	RD15	RD15-2
Plain rice	RD15	RD15-3
Plain rice	RD15	RD15-4
Plain rice	RD15	RD15-5
Plain rice	RD15	RD15-6
Plain rice	RD15	RD15-7
Plain rice	RD15	RD15-8
Plain rice	RD15	RD15-9
Plain rice	RD15	RD15-10
Plain rice	RD15	RD15-11
Plain rice	RD15	RD15-12
Plain rice	RD15	RD15-13
Glutinous rice	RD14	RD14-1
Plain rice	RD15 Pitsanulok	RD15-PIT-1
Plain rice	RD15 Pitsanulok	RD15-PIT-2
Glutinous rice	Phayao black rice	PBR-1
Glutinous rice	Phayao black rice	PBR-2
Crossed breed between black rice and white jasmine rice	Riceberry	RB
Plain rice	RD15 white jasmine rice 105	RD15-KDM 105
Glutinous rice	RD6 Thai Prathumthani fragrance rice	RD6-TPFR
Glutinous rice	RD16	RD16-1

Table 2: The type of rice samples, mutant name and the codes.

Statistical Analyses

The statistical analyses were performed using IBM SPSS Statistic version 21.0.

Results and Discussion

Arsenic in Rice

The concentrations of arsenic in the 43 unpolished rice samples are shown (Figure1) and as far as can be ascertained, the rice samples were grown in uncontaminated soil where there was no history of industrial pollution.

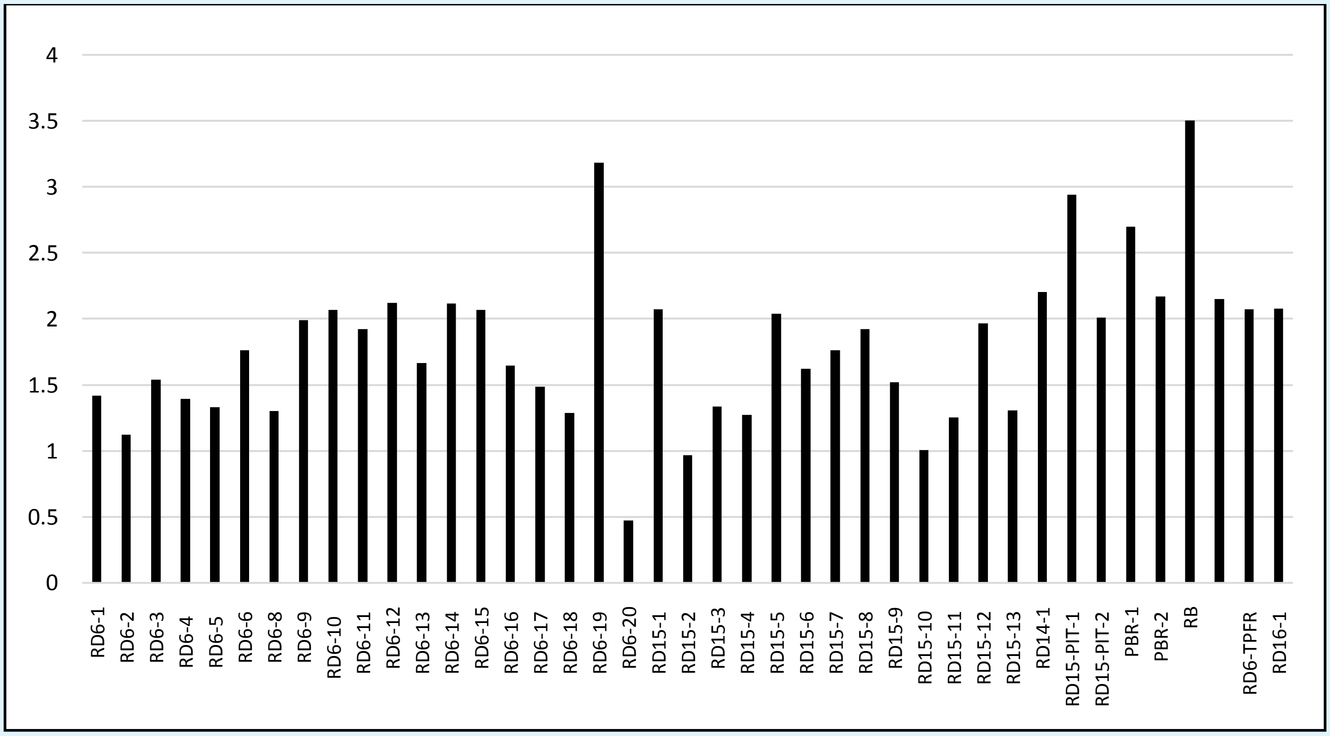

Figure 1: Arsenic concentrations in the rice samples (ppb)*.
*(1ppb = 0.001 mg kg^{-1})

At a glance, it is apparent that all the rice samples contained some arsenic. The mean, range and standard deviation are given in (Table 3).

Samples	Number (*N*)	Concentration (ppb)
Mean	43	1.8
Range	43	Minimum-Maximum 0.5-3.5
Standard deviation	43	0.6

Table 3: Mean, range and standard deviation of arsenic in rice.

The range for arsenic content in the rice is 5.0x10^{-4} – 3.5x10^{-3} mg kg^{-1} (0.5-3.5 ppb) with the mean of 1.8 x10^{-3} mg kg^{-1} (1.8 ppb) and a standard deviation of 0.6. As seen in (Figure 2), two rice samples contained the highest of arsenic concentrations of 3.5x10^{-3} mg kg^{-1} (3.5 ppb) in RB and 3.2x10^{-3} mg kg^{-1} (3.2 ppb) in RD6-19.

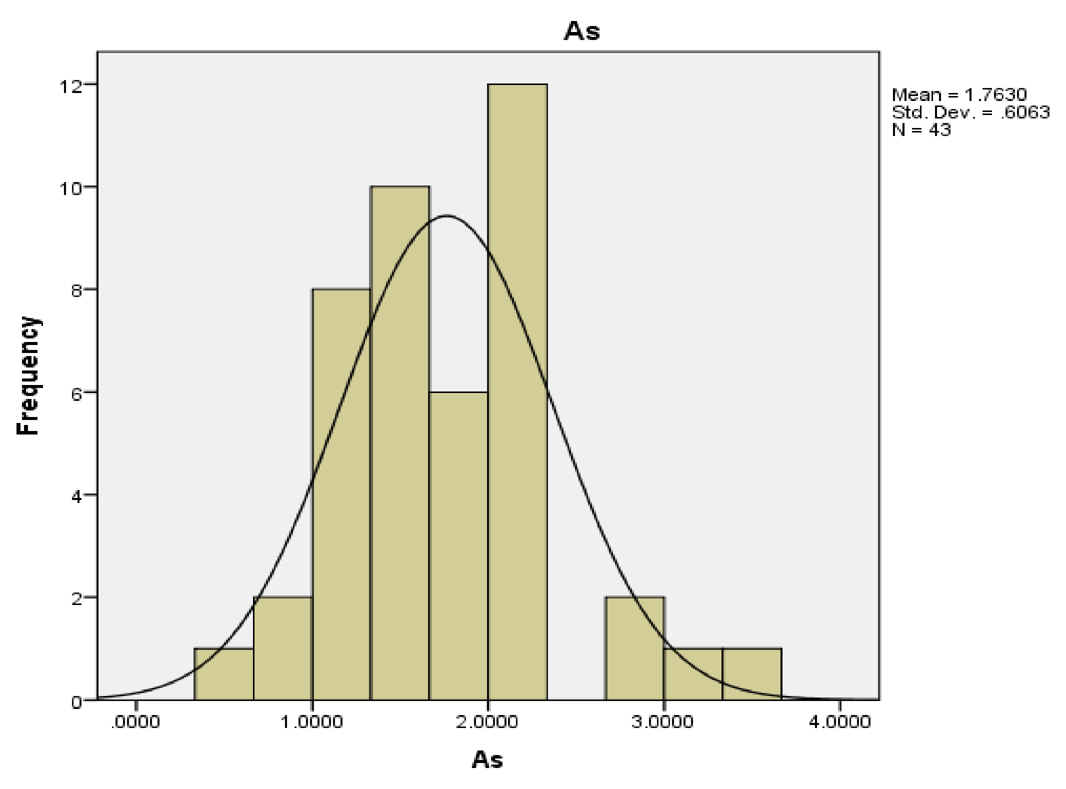

Figure 2: Standard deviation for arsenic in rice.

The results indicate that the level of arsenic in all the rice samples was well below the guideline value of 0.2 mg/kg (200 ppb) agreed by Codex Alimentarius for arsenic in white rice [21]. Based on the results in this study, the arsenic concentrations are relative low compared with the data from Consumer reports, 2012 and [21]. The present study also showed that arsenic contents and the range in the samples are much lower when comparing with the Chinese limits which are permitted at 0.2 mg kg^{-1} for arsenic in rice grains [27]. In the European Union (EU), setting a maximum limit of 0.4 mg kg^{-1} (400 ppb) for arsenic in brown rice was discussed [28]. In terms of arsenic contamination in other foods, many studies have detected high levels of arsenic in rice based products such as rice milk, rice bran, rice-based breakfast cereals, rice cereal bars containing rice and rice crackers. A study was carried out by [29] on baby rice, rice cereal and rice crackers. The results showed some samples contained a higher level of inorganic arsenic than the advisable maximum limit of 0.20 mg kg^{-1} (200 ppb) for arsenic in white rice by [21]. In another study [30] showed that some Spanish gluten-free baby rice based products have elevated inorganic arsenic concentration, ranging from 126 ± 26 mg kg^{-1}. They suggested that babies particularly those aged from 6-12 months old have a high potential to be exposed to arsenic when fed with 3 portions of rice cereal per day mixed with water containing 10 mg l^{-1} of arsenic.

At present, in the Europe Union, the maximum levels of inorganic arsenic in foodstuff has been set by the Commission Regulation [22] (EU) no 2015/1006, amending Regulation (EC) No 1881/2006) setting maximum levels for certain contaminants in foodstuffs (European Commission, 2015). Comparing the mean of arsenic concentrations in the samples and the maximum levels for arsenic in non-parboiled milled rice (polished or white rice), the mean arsenic concentration $1.8x10^{-3}$ mg kg^{-1} in the samples was far less than the European Commission guideline of 0.20 mg kg^{-1}. According to the [31], Thai regulations specify the maximum limits for heavy metals such as inorganic arsenic but only for fish and sea foods. The Thai limits stated that the acceptable level for arsenic in fish and seafood is 2 mg kg^{-1} and 2 mg kg^{-1} for total arsenic in other foods set by the Ministerial Notification No. 98 of B.E. 2529 (1986) and Ministerial Notification No. 273 of B.E. 2546 (2003). In some countries like Australia and New Zealand, the total maximum allowable arsenic level for cereal and rice is suggested at 1 mg kg^{-1} [32-38]. With regards to arsenic, it can conclude that it is statistically highly significant as $P < 0.001$. The P-value in rice is 0.00.

Conclusion

Rice, one of the most widely consumed foods in the world, is also one of nature's great scavengers of metallic compounds. Consumers have already become alarmed over reports of rice-conveyed arsenic in everything from cereal bars to baby foods. This study found that arsenic was present in all the rice samples but the concentrations were lower than the limits (0.20 mg kg^{-1} to 0.30 mg kg^{-1}) or guideline value (0.20 mg kg^{-1}) set by the European Union and the Codex Alimentarius, respectively. Thus it can be concluded that the rice samples studied, are compliant and consequently pose a minimum threat to human health. However, further studies may be required to investigate the potential for hazardous levels of arsenic in rice from different parts of Thailand, from contaminated soils and rice samples treated with chemical fertilizers.

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