REGULAR ARTICLE

Quantification of aluminum and heavy metal contents in cooked rice samples from Thailand markets using inductively coupled plasma mass spectrometry (ICP-MS) and potential health risk assessment

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ABSTRACT

This work quantified contents of Al and heavy metals, namely Cr, Fe, Cu, Zn, As, Cd, and Pb, in cooked rice samples prepared using five different cooking utensils (new and used Al cookers, a Teflon-coated Al cooker, a stainless steel cooker, and a glass beaker) and four different water conditions (tap water, de-ionized water, acidic water, and basic water) in order to assess metal leaching from cooking utensils and potential health risks to local consumers. The result showed that Al contents (76.50 mg kg^{-1} in raw rice and 76.83 mg kg^{-1} in cooked rice samples) and Zn contents (22.86 mg kg^{-1} in raw rice and 22.43 mg kg^{-1} in cooked rice samples) represented the two largest contents of tested elements, in which contents of Al > Zn > Fe > Pb ≈ Cu > Cr > As ≈ Cd. However, no strong indication of substantial metal leaching from cooking utensils to cooked rice were observed in this work as the metal contents in cooked rice samples did not significantly differ from raw rice grains ($p < 0.05$). The result also indicated that the estimated weekly intake of Al and Pb associated with rice consumption of a person who consumed approximately 0.3 kg of rice per day (181.07 mg kg^{-1} week^{-1} and 4.85 mg kg^{-1} week^{-1}, respectively) was greater than the provisional tolerance weekly intake (PTWI) recommended by the joint FAO/WHO committee for a person who weighs 60 kg (120 mg kg^{-1} week^{-1} and 1.5 mg kg^{-1} week^{-1}, respectively). In terms of the assessment of non-carcinogenic and carcinogenic health risks, the hazard index (*HI*) calculated from all concerned metals was 9.18, with the largest contributions from Pb (3.19), As (2.67), and Al (1.51), indicating a potential non-carcinogenic risk, while the total cancer risk (*CRt*) was 2.45×10^{-2}, with the largest contributions from Pb (1.0×10^{-2}) and Cd (1.2×10^{-2}), indicating serious carcinogenic risks to local consumers.

Keywords: Aluminum; Food safety; Health risks; Heavy metal; ICP-MS; Rice

INTRODUCTION

Rice (*Oryza sativa*) is one of the most consumed foods in the world, especially in southern and eastern Asia, due to its abundant nutrients and favorable taste. It was estimated that Asia's per capita rice consumption had increased from 85 kg per year in the early '60s to 103 kg per year in the early '90s, while the global per capita consumption rose from 50 to 65 kg per year during the same period. Furthermore, rice consumption and production are anticipated to keep growing due to the rapid increase in the world's population, improved nutrition in rice, and better harvesting technologies (Mohanty, 2013).

Rice grains have a high carbohydrates content, with small amounts of protein and fat, making them one of the most important sources of energy and nutrition for humankind. Rice also contains many useful substances including Omega-3 and Omega-6 fatty acids that are important components of cell membranes that help to regulate blood pressure and inflammatory response. However, elements such as aluminum (Al) and heavy metals (arsenic: As, cadmium: Cd, iron: Fe, lead: Pb, zinc: Zn, copper: Cu, and chromium: Cr) in rice grains could pose a serious health risk to consumers.

In the case of Al, which is the third most abundant element in the earth's crust, several medical reports

have linked its excessive daily intake to possible causes of brain, blood, and bones diseases (Al Zubaidy et al., 2011), especially Alzheimer's disease, for which it has been reported that residual aluminum in drinking water plays an important role in developing the disease (Becaria et al., 2006; McLachlan et al., 1996; Flaten, 2001; Crapper et al., 1966). In raw rice, the Al content was measured to be from as little as a few mg kg^{-1} up to 350 mg kg^{-1} depending on the rice type, growing region, and measurement method (Semwal et al., 2006; Odularu et al., 2013). The World Health Organization (WHO) reported in 1989 that the provisional tolerance weekly intake (PTWI) of Al was not more than 7 mg kg^{-1} of body weight (World Health Organization, 1989) and later this was revised to 1 mg kg^{-1} of body weight and 2 mg kg^{-1} of body weight in 2006 and 2011, respectively (Center for Food Safety, 2009; World Health Organization, 2011). This means that a person weighing 60 kg could have a maximum Al intake of 120 mg per week according to the WHO report. As a consequence, from previous reports, a moderate person who consumes roughly 1-2 kg of rice per week could be at a serious health risk of excessive aluminum intake, with even greater effects for people living in southern and eastern Asia.

In addition to the risks from Al intake, heavy metals such as As, Cd, Fe, Pb, Zn, Cu, and Cr are also posing threats to consumer's health. Table 1 shows the possible health effects of these heavy metals, for both acute and chronic exposures, and the PTWI of each element recommended by the joint FAO/WHO committee. Zeng et al. (2015) used atomic absorption spectrometry (AAS) to show that raw brown rice in Hunan Province, China, contained Cd (0.325 mg kg^{-1}), Cr (0.109 mg kg^{-1}), As (0.344 mg kg^{-1}), Ni (0.610 mg kg^{-1}), Mn (9.03 mg kg^{-1}), Pb (0.023 mg kg^{-1}),

and Hg (0.071 mg kg^{-1}), which indicated that long-term exposure to heavy metals through brown rice consumption posed both potential non-carcinogenic and carcinogenic health risks to the local residents.

In addition to health risks from Al and heavy metals intake from rice grains, possible leaching from cooking utensils, especially rice cookers, could potentially add more metals to raw rice and pose greater health effects. This possibility of leaching has led to several attempts to clarify the safety of rice cookers. Odularu et al. (2013) investigated possible leaching of Al from aluminum, clay, stainless steel, and steel cooking pots using colorimetry and the aluminon method at 550 nm. The results showed that rice cooked in an aluminum pot had the content of Al ranging from 126 mg kg^{-1} to 314 mg kg^{-1}. Another study using a UV spectrometer and the aluminon method at 530 nm performed by Amarasooriya et al. (2014) indicated that rice cooked in the presence of aluminum plate without fluoride water resulted in an additional 6.5 mg kg^{-1} of Al in rice and the Al contents increased as the fluoride concentration in the water increased. This possible leaching of Al could affect consumers' health as shown by Ileperuma et al. (2009) that the dissolution of Al from utensils under high fluoride stress could be a possible risk factor for chronic renal failure in the North-Central Province in Sri Lanka. On the other hand, Omar et al. (2015) investigated the bioavailability of heavy metals in cooked rice using an *in vitro* digestion model and inductively coupled plasma optical emission spectrometry (ICP-OES). The results indicated that cooked rice contained Cr (0.11±0.01 mg kg^{-1}), Cd (0.031±0.001 mg kg^{-1}), Cu (1.1±0.1 mg kg^{-1}), Fe (1.9±0.1 mg kg^{-1}), and Zn (4.3±0.1 mg kg^{-1}), leading to high cancer risks for both adults and children.

Table 1: Possible health effects of heavy metals and their PTWI levels recommended by the WHO. (World Health Organization, 2011; Occupational Safety and Health Administration, 2013). Numbers in parentheses represent PTWI values before the limits were withdrawn

Element	Health effects	Provisional tolerance weekly intake (PTWI) (mg kg^{-1} of body weight)
Arsenic (As)	Discoloration of the skin, appearance of small corns or warts, and death.	(0.0147)[a]
Cadmium (Cd)	Flu-like symptoms, kidney, bone, and lung disease.	0.006
Iron (Fe)	Irritant to the lungs and gastrointestinal tract, siderosis, and interstitial disease.	5.6
Lead (Pb)	Impaired kidney function, high blood pressure, nervous system and neurobehavioral effects, subtle cognitive effects attributed to prenatal exposure.	(0.025)[b]
Zinc (Zn)	Copper deficiency and dermatitis following prolonged skin exposure.	2.1-7.0
Copper (Cu)	Cumulative lung damage.	3.5
Chromium (Cr)	Cancer and damage to respiratory system, kidneys, liver, skin, and eyes.	0.0233

[a]The previously established PWTI of 14.7 µg kg^{-1} of body weight was no longer health protective as the Benchmark Dose Lower Confidence Limit (BMDL0.5) value was in the same range as the PTWI value (World Health Organization, 2011).

[b]The previously established PWTI of 25 µg kg^{-1} of body weight was withdrawn because the experts found it was not possible to establish a new PTWI that would be considered health protective (World Health Organization, 2011)

Despite the availability of information on Al and heavy metal contents in rice samples, previous methods used for the analysis could have disadvantages that led to inaccurate results and difficult interpretation. For example, similar wavelengths of light emitted from different elements or matrix interferences could affect analysis in the colorimetry method. To overcome these constrains, inductively coupled plasma mass spectrometry (ICP-MS), which has equal or better detection limits for most elements than AAS, colorimetry, and ICP-OES, with simultaneous multi-element measurement ability, was selected as an analytical tool in this work (Horn, 2000; Whitea, 2000). Another important justification of this work was that, in contrast to Al, information of heavy metal leaching from cooking utensils during rice cooking was lacking and insufficient as seen by a small number of heavy metal species and reports. An example of heavy metal leaching study was the measurement of Ni and Cr leaching from a stainless steel pot into tomato sauces, which showed slight increases in Ni and Cr contents after cooking (Kamerud, 2013).

As a result, we aimed to quantify the Al and heavy metal (Cr, Fe, Cu, Zn, As, Cd, and Pb) contents using ICP-MS in both raw rice and cooked rice samples that were prepared using five different rice cooking utensils (new and 3-year-old Al cookers, a Teflon-coated Al cooker, a stainless steel cooker, and a laboratory glass beaker) and four different water conditions (tap water, de-ionized water, acidic water, and basic water). The contents of all concerned metals obtained from the measurement were then analyzed in order to assess any significant level of metal leaching and any potential health risk to local consumers. Overall results from this work would be greatly useful for both policymakers, producers, and consumers to raise food safety awareness associated with rice consumption.

MATERIALS AND METHODS

Instruments and apparatus
An electrically heated oven (Binder: Model ED/FD, USA) ventilated naturally and by fan-assisted circulation and a laboratory agate gyro mill (Glen Creston, USA) were used for sample milling and digestion. Rice samples were cooked using four 1-L commercial rice cooking utensils that were made from different materials—new and 3-year-old Al (New-Al and Old-Al, respectively), Teflon-coated Al (Tef-Al), stainless steel (SS)—and one reference cooker (a laboratory glass beaker; Gl). It should be noted that all cooking utensils were cleaned by distilled water and a commercial dishwasher and left to dry in an open air. The powdered rice samples were kept in sealed polyethylene (PE) bags at -16°C using a medical refrigerator (EVERMed: Model LCDF 220 W, Italy), while the rice samples in solvents prepared for ICP-MS analysis were stored in high-density polyethylene bottles. Table 2 shows the operating parameters of the ICP-MS machine and settings used for the elemental analysis. The detection limits for all concerned elements were 20 ng L^{-1} except for Fe that had a detection limit of 900 ng L^{-1}.

Reagents
All reagents including HNO_3, HCl, and NaOH (Merck Millipore, Thailand) for sample digestion and water preparation were of analytical-reagent grade. The water used in this work, unless note otherwise, was doubly de-ionized using a Milli-Q water purification system (Millipore, USA). Plastic materials were cleaned by soaking in 10% (v/v) HNO_3 for 24 hr, rinsing with de-ionized water and dry under a class 100 laminar flow hood, which was also used during sample digestion.

Sample preparation
Three different brands of white rice grown in central Thailand were purchased in a local grocery store in Bangkok. Four types of water—regular tap water (TW), de-ionized water (DW), acidic water (AW) and basic water (BW) were used to cook rice samples. For TW, normal running water in households supplied by the Thailand Metropolitan Waterworks Authority (MWA) was used. For AW, 1 mL of 6M HCl was mixed with 200 mL of DW and continuously stirred in a 250 mL laboratory beaker. Then, 3.35 mL of the strong acidic solution was transferred and diluted with DW in a 1000 mL measuring cylinder

Table 2: ICP-MS machine model (Agilent 7500a and 7500c) and operating parameter settings

Operating parameter	Setting
Spray chamber type	Scott double pass, 2±0.1°C
Nebulizer type	Babbington high solids nebulizer
RF power (W)	1350 W (7500a), 1500 W (7500c)
Carrier gas flow rate (L min^{-1})	1.08
Make-up gas flow rate (L min^{-1})	0.00
Data acquisition mode	Spectrum analysis mode and full quant mode
Torch	Fassel
Sample depth	7.0 mm
Integration time (ms)	300 for As, Zn, Cr, and Al and 100 for Fe, Cd, Cu, and Pb

until the pH of the AW was approximately 4.0±0.3. For BW, 0.4 g of NaOH was mixed with DW and stirred in a 1000 mL measuring cylinder until the pH of the BW was approximately 10.0±0.3. To determine whether the water used during rice cooking could contribute significant amounts of Al and heavy metals to the rice samples, 5 mL of each water type was individually analyzed using the same ICP-MS setup and procedures. The results indicated that the Al and heavy metal contents in all types of water were substantially less than 1 mg kg^{-1}; hence, they contributed negligibly to the final elemental contents in the cooked rice samples.

To prepare cooked rice samples, all 20 possible combinations were tested using 432 g of each rice sample separately cooked with 600 mL of each water type in each of the five rice cookers. The cooked rice samples were then oven-dried at 65°C for 48 hr and ground to fine powder using the laboratory agate gyro mill. The cooked rice powder samples were sealed in PE bags and kept at -16°C for sample digestion. For reference purposes, raw rice grains were also oven-dried, ground, and kept in PE bags following the same procedures used for the cooked rice samples.

To perform sample digestion, powder samples weighing 0.50±0.01 g were added to 5 mL of (65% w/w) HNO$_3$ and left for 30-40 minutes. The samples were then heated using a hot plate with a magnetic stirrer at 95°C for 2 hr. Another 5 mL of (65% w/w) HNO$_3$ was later added to the samples and heated again at 95°C for 2 hr. The samples were then left to cool and the volume was made up to 50 mL in a volumetric flask using de-ionized water. To perform ICP-MS analysis, 5 mL of each digested rice sample was transferred to a measuring cylinder and tested under the settings shown in Table 2. The sample IDs used to identify rice samples under different conditions were the synonym of cooker types followed by the synonym of water types used in rice cooking. For example, a rice sample that was cooked in the 3-year-old Al rice cooker with DW would be noted as Old-Al-DW.

Quality assurance and quality control
The spike recovery test was performed to validate and to assess the accuracy of ICP-MS in elemental analysis. To perform the spike recovery test, an uncooked rice sample was divided into two sets and digested using the same procedures outlined in the sample preparation section. One of the two 50 mL rice samples was added with 1 mL of the environmental calibration standard (Agilent Part Number 5183-4688, USA) that contained known amounts of elements of interest (20,000 µg L^{-1} for Fe and 200 µg L^{-1} for other elements). Both spiked and unspiked samples were then analyzed using ICP-MS.

The percentages of spike recovery for each element were calculated using the equation

$$\% \, Recovery = [(Observed - Neat)/Expected] \times 100\% \qquad (1)$$

where *Observed, Neat,* and *Expected* are the element contents in spiked samples, the element contents in unspiked samples, and the known amount of standard that was spiked into the sample, respectively. Since the acceptable percentage of recovery depends on the concentration and species of the element of interest, the acceptable percentage of recovery in our work, in which the element contents were expected to be in the range 0.1-100 mg kg^{-1}, needed to be in the range of 80-120%.

The results of the spike recovery test showed that the range of the percentage recovery was between 86.17% - 106.11%, indicating sufficient accuracy of the elemental determination of ICP-MS to extract reliable and accurate information.

Statistical analysis and validation of method
A level of 95% significance (p<0.05) was used for the descriptive analysis of data. The t-test was also applied to determine any significant difference between each condition of cooked rice samples.

Health risk assessment
Non-carcinogenic and carcinogenic risks from rice consumption were evaluated to characterize the health risks due to exposure to the toxicants in the cooked rice. The non-carcinogenic risk was determined using the hazard quotient (*HQ*), which is the ratio of the potential exposure to a substance and the level at which no adverse effects are expected, and can be calculated as (Zeng et al., 2015)

$$HQ = ADI/RfD \qquad (2)$$

where *ADI* and *RfD* are the average daily intake and the reference dose issued by the Integrated Risk Information System (IRIS), respectively (Zeng et al., 2015). If *HQ* is less than 1, adverse health effects would be unlikely to occur. On the other hand, if *HQ* is greater than 1, potential non-carcinogenic effects could occur (Nuapia et al., 2018). In this work, *HQ* was calculated based on (Zeng et al., 2015)

$$ADI = C \times IR \times ED \times EF/BW \times AT \qquad (3)$$

where *C, IR, ED, EF, BW,* and *AT* are the metal content (mg kg^{-1}) in cooked rice, the ingestion rate (kg d^{-1}), exposure duration (d), exposure frequency (y), body weight (kg), and average time (d) respectively. The *IR, ED, EF, BW,* and *AT* values used in this work were 0.3 kg d^{-1}, 365 d, 75 y, 60 kg, and 27,375 d, respectively, based on the average rice consumption rate in Thailand reported by the Office of Agricultural Economics, Thailand Ministry of Agriculture and Cooperatives, the life expectancy at birth reported by

the World Health Organization (2015), and the average weight of Thai adults reported by Charoensitiwath (2010).

Another indication of non-carcinogenic health risk caused by a mixture of toxicants is provided by the hazard index (*HI*), which was calculated as (Zeng et al., 2015)

$$HI = \Sigma HQ \qquad (4)$$

For cases where *HI* > 1, chronic risks are likely to occur.

In terms of carcinogenic risks, the cancer risk (*CR*) of a carcinogenic element, which represents the incremental probability of an individual to develop cancer over a lifetime, was evaluated as (Zeng et al., 2015)

$$CR = ADIXCSF \qquad (5)$$

where *CSF* is the cancer slope factor of element of interest. In this work, only the oral intake of relevant metals would be of interest in the carcinogenic risk assessment. If multiple carcinogenic elements are present, the total cancer risk (*CRt*) could be calculated as (Zeng et al., 2015)

$$CRt = \Sigma CR \qquad (6)$$

CRt values in the range 1.0×10^{-6} to 1.0×10^{-4} are considered acceptable for carcinogenic risk, while a *CRt* value greater than 1.0×10^{-4} indicates possible carcinogenic risk (Cao et al., 2015) The values of *RfD* and *CSF* for each element are shown in Table 3.

RESULTS AND DISCUSSION

Elemental analysis in raw and cooked rice samples
Values of elemental contents in raw and cooked rice samples are shown in Table 4 and Table 5. The results showed that Al and Zn represented the two largest contents

of tested elements in both raw and cooked rice, in which the average contents of Al > Zn > Fe > Pb ≈ Cu > Cr >As ≈ Cd (p<0.05).

The contents of Al in rice samples found in this work ($49.19 - 115.16$ mg kg^{-1}) were in between the reported values of Odularu et al. (2013), Omar et al. (2015), and Semwal et al. (2006), in which the former report showed the Al contents of 126 ± 64 mg kg^{-1}, 314 ± 128 mg kg^{-1}, and 295 ± 163 mg kg^{-1} for samples cooked in a new Al cooker, a used Al cooker, and a SS cooker, respectively, while the latter two reports showed the Al contents between $0.67 - 1.5$ mg kg^{-1}. The large variations in Al contents found in this work and other works could be due to the differences in rice types, growing regions, and the accuracy of testing methods used to quantify Al contents. For heavy metal contents, the values found in this work were in agreements with the previous work of Zarcinas et al. (2004) who investigated heavy metals contents in soils and crops in Thailand. The report indicated that Zn had the highest contents in rice samples (22.8 mg kg^{-1}) compared to As (<1 mg kg^{-1}), Cd (0.05 mg kg^{-1}), Cr (0.7 mg kg^{-1}), Cu (2 mg kg^{-1}), and Pb (0.11 mg kg^{-1}). The results were also similar to the reports of Zeng et al. (2015), who showed that the heavy metal contents in brown rice samples cultivated in Human Province, China, had Cd (0.325 mg kg^{-1}), Cr (0.109 mg kg^{-1}), As (0.344 mg kg^{-1}), and Pb (0.023 mg kg^{-1}). Furthermore, the comparison of heavy metal contents in this work and the official limits of selected toxicants in foods released by the Thailand Ministry of Public Health in 1986 and 2003 showed that the values found in this work were lower than the limits (Zn < 100 mg kg^{-1}, Cu < 20 mg kg^{-1}, and As < 2 mg kg^{-1}). Another interesting result was that Zn had the highest contents amongst all tested heavy metals. This could be because the soil-to-plant transfer factors (TF) in rice of Zn was relatively high (0.96), leading to a high transfer from soil to plant and a high accumulation of Zn in rice

Table 3: Carcinogenic classification by International Agency for Research on Cancer (IARC), reference doses (*RfD*) and oral cancer slope factors (*CSF*) of metals of interest (Integrated Risk Information System, 2017; Zeng et al., 2015)

Element	Weight of evidence (WOE) characterization[a]	*RfD* (mg kg^{-1} d^{-1})	*CSF* (mg^{-1} kg d)
Al	N/A	0.286[b]	-
Cr	N/A	0.003	0.5
Fe	D	0.8	-
Cu	D	0.5[b]	-
Zn	N/A	0.3	-
As	A	0.0003	1.5
Cd	B1	0.001	15
Pb	B2	0.0036[b]	0.91

[a]International Agency for Research on Cancer: group A chemicals are definite human carcinogens; group B1 chemicals are probable human carcinogens based on limited evidence of carcinogenicity in humans; group B2 chemicals are probable human carcinogens based on sufficient evidence of carcinogenicity in animals; and group D chemicals are not classifiable regarding human carcinogenicity. N/A indicates IRIS had inadequate information to assess carcinogenic health risks from oralintake of that element. [b]RfD values were not available through IRIS. They were estimated using the PTWI values in Table 1.

Table 4: Al, Cr, Fe, and Cu contents in raw and cooked rice samples prepared using different rice cookers and water types. Values are represented as mean±standard deviation

Samples	Content (mg kg^{-1})			
	Al	Cr	Fe	Cu
Raw Rice	76.49±19.72	0.27±0.03	4.90±0.42	1.79±0.26
New-Al-TW	76.83±9.47	0.28±0.01	4.06±0.33	1.76±0.55
New-Al-DW	93.37±8.69	0.31±0.04	3.95±0.22	1.91±0.34
New-Al-AW	107.61±26.16	0.34±0.09	3.75±0.55	1.72±0.65
New-Al-BW	62.77±4.95	0.10±0.01	4.11±0.31	1.72±0.62
Old-Al-TW	92.91±7.35	0.35±0.01	3.74±0.46	2.59±0.25
Old-Al-DW	85.04±13.08	0.68±0.05	3.81±1.80	1.78±1.37
Old-Al-AW	44.34±0.70	0.27±0.04	2.04±0.01	1.63±0.67
Old-Al-BW	74.93±0.02	0.13±0.02	4.11±0.70	1.86±0.19
Tef-Al-TW	83.34±11.31	0.30±0.03	3.69±1.48	1.39±0.17
Tef-Al-DW	104.01±9.89	0.41±0.01	7.34±1.06	2.13±1.16
Tef-Al-AW	115.16±11.41	0.32±0.03	2.67±0.18	1.47±0.91
Tef-Al-BW	71.42±3.11	0.28±0.05	2.88±0.77	1.31±0.72
SS-TW	91.85±4.17	0.34±0.02	6.48±0.24	1.66±0.83
SS-DW	84.99±12.79	0.37±0.01	2.80±0.14	1.99±0.33
SS-AW	98.35±20.85	0.37±0.04	2.95±0.18	1.62±0.47
SS-BW	111.03±15.55	0.25±0.04	3.15±0.19	1.76±0.65
Gl-TW	105.21±11.14	0.44±0.13	3.22±1.52	2.21±0.29
Gl-DW	80.78±14.99	0.14±0.02	5.69±0.41	2.23±0.19
Gl-AW	56.00±9.98	0.15±0.01	3.09±0.35	1.58±0.25
Gl-BW	49.19±9.61	0.18±0.01	4.55±0.74	1.62±0.16

Table 5: Zn, As, Cd, and Pb contents in raw and cooked rice samples prepared using different rice cookers and water types. Values are represented as mean±standard deviation

Samples	Content (mg kg^{-1})			
	Zn	As	Cd	Pb
Raw Rice	22.85±6.86	0.14±0.01	0.11±0.12	1.36±0.65
New-Al-TW	27.58±7.65	0.15±0.03	0.24±0.07	3.83±0.18
New-Al-DW	24.47±7.65	0.14±0.02	0.18±0.03	1.98±0.16
New-Al-AW	24.57±4.56	0.20±0.01	0.15±0.03	2.27±0.19
New-Al-BW	25.83±1.90	0.16±0.02	0.16±0.03	1.76±0.16
Old-Al-TW	26.25±2.22	0.15±0.03	0.09±0.02	1.66±0.13
Old-Al-DW	26.46±3.00	0.15±0.04	0.15±0.03	1.84±0.05
Old-Al-AW	24.57±1.02	0.19±0.01	0.15±0.01	2.30±0.06
Old-Al-BW	23.42±3.16	0.16±0.02	0.05±0.01	1.41±0.18
Tef-Al-TW	22.52±2.74	0.15±0.03	0.12±0.01	1.76±0.15
Tef-Al-DW	26.50±3.22	0.21±0.02	0.15±0.04	2.63±0.33
Tef-Al-AW	24.08±1.63	0.21±0.02	0.17±0.03	2.28±0.16
Tef-Al-BW	26.88±0.85	0.18±0.03	0.05±0.05	1.11±0.04
SS-TW	22.42±5.77	0.15±0.01	0.13±0.04	1.96±0.26
SS-DW	30.61±3.33	0.20±0.04	0.20±0.02	2.66±0.20
SS-AW	31.32±0.61	0.21±0.02	0.19±0.01	2.39±0.06
SS-BW	21.41±0.56	0.19±0.01	0.05±0.01	1.06±0.04
Gl-TW	24.76±1.25	0.16±0.06	0.04±0.01	1.81±0.12
Gl-DW	22.94±5.79	0.17±0.02	0.03±0.01	1.82±0.16
Gl-AW	26.08±1.82	0.15±0.02	0.01±0.01	1.38±0.12
Gl-BW	30.26±2.38	0.15±0.03	0.03±0.01	0.86±0.06

grains. Note that the average Zn contents in all types of soil in Thailand was reported to be 23.9 mg kg^{-1}, close to the Zn contents in rice samples (Zarcinas et al. 2004).

In terms of the differences in Al and heavy metal contents in raw rice samples and cooked rice samples, the results showed that, although there were some fluctuations in values of elemental contents in different rice samples, the t-test at 95% significant level implied that the values were not significantly different and were statistically inconclusive to draw any conclusion that significant metal leaching was found in this work. The same statistical results that showed insignificant different between rice samples were also found in all conditions. This could be because the variations in rice cooking conditions used in this work might not be sufficient to initiate or to show significant amount of metal leaching as reported by Al Zubaidy et al. (2011) that the leaching of Al from Al cookware was dominant when the pH of the water used in cooking was lower than 3 or higher than 10, leading to insignificant leaching of metal in rice samples cooked with AW (pH = 4.0) and BW (pH = 10.0) in this work. Another reason that could also reduce possibility of metal leaching into food during the cooking process was the increase in rice cooker safety standards and also the advances in manufacturing (Underwriters Laboratories Inc., 2017).

Another interesting point to consider was the estimated weekly intake of Al and heavy metals by rice consumers. Table 6 shows the minimum, maximum, and estimated weekly intake of a person who consumes 0.3 kg per day of white rice prepared using four types of rice cookers (Old-Al, New-Al, Tef-Al and SS) with TW. The estimated weekly intake for each element was then compared with the PTWI of a person weighing 60 kg. The results showed that the estimated weekly intakes of for Al and Pb were higher than PTWI, indicating long-term exposure effects to local consumers. However, the updated PTWI values of Pb have not yet been issued by the WHO due to inadequate information to establish health protective levels; hence, reliable conclusions for Pb cannot be drawn until further information becomes available.

Health risk assessment

The *ADI*, *HQ*, and *CR* values for each heavy metal calculated from the estimated weekly intakes (Table 6) are shown in Table 7.

The *HQ* values through rice consumption as shown in Table 7 indicate that Al, As and Pb individually posed potential non-carcinogenic risks as their values were greater than 1. Furthermore, the *HI* value calculated from all metals was 9.18, implying high chronic health risks from rice consumption. The estimated *HI* was mainly due to the Pb and As contents, which accounted for 34.7% and 29.1% of the *HI*, respectively. The contributions from all concerned metals to the *HI* value are shown in Fig 1. In terms of *CR* and *CRt* values, Cd, Pb, As, and Cr had *CR* values greater

Table 6: Minimum, maximum, estimated weekly intake, and Provisional tolerance weekly intake values of elemental contents in cooked rice samples prepared using four commercial rice cookers and TW. Numbers in parentheses represent PTWI values before the limits were withdrawn
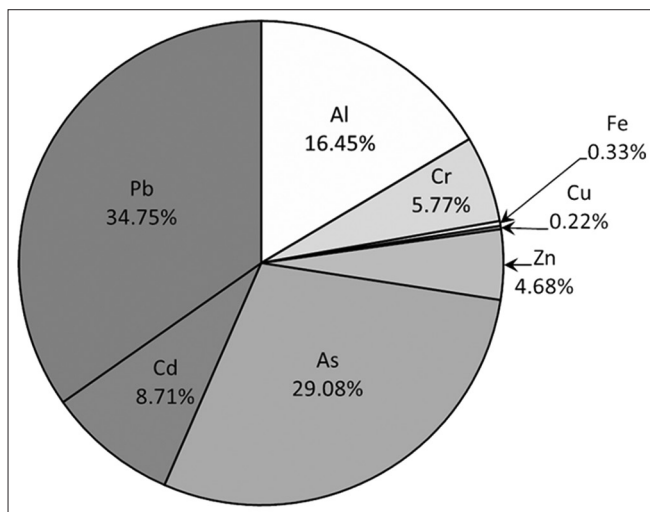
Element	Content (mg kg⁻¹)		Estimated weekly intake (mg) [a]	Provisional tolerance weekly intake (mg) [b]
	Minimum	Maximum		
Al	76.83	92.91	181.07	120
Cr	0.28	0.35	0.67	1.398
Fe	3.66	6.4	9.45	336
Cu	1.39	2.59	3.89	210
Zn	22.42	27.55	51.87	126-420
As	0.15	0.15	0.32	(0.882)
Cd	0.09	0.24	0.32	0.36
Pb	1.66	3.83	4.85	(1.5)

[a]For a person who consumes roughly 2.1 kg of rice per week (0.3 kg of rice per day).
[b]For a person weighing 60 kg

Table 7: Average daily intakes (*ADI*), hazard quotient (*HQ*), and cancer risk (*CR*) of metals in cooked rice

Element	Average daily intakes; *ADI* (mg kg⁻¹ d⁻¹)	Hazard quotient; *HQ*	Cancer risk; *CR*
Al	0.4311	1.51	-
Cr	0.0016	0.53	8.0×10^{-4}
Fe	0.0225	0.03	-
Cu	0.0093	0.02	-
Zn	0.1235	0.43	-
As	0.0008	2.67	1.7×10^{-3}
Cd	0.0008	0.80	1.2×10^{-2}
Pb	0.0115	3.19	1.0×10^{-2}

Fig 1. Hazard index (HI) contributed by each metal of interest.

than 10^{-4}, leading to *CRt* of 2.45×10^{-2}, which indicated high carcinogenic risks from rice consumption. Fig 2. shows the contributions of all metals of interest to *CRt*. These results were similar to reports by Zeng et al. (2015) which indicated that long-term exposure to heavy metals through brown rice consumption posed both potential non-carcinogenic and carcinogenic health risks to the local residents in Hunan Province, China, and by Sinha et al. (2015), which indicated excessive As toxicity in rice with special reference to speciation in Indian grain that led to risks associated with consumption of As contaminated rice.

In summary, rice consumption could pose serious health risks to consumers—through both non-carcinogenic and carcinogenic effects—from Al and heavy metal contents. Furthermore, when other intake pathways such as inhalation and dermal exposure and other types of foods such as fish, vegetables, and water are taken into consideration, the potential health risks could be greatly increased. Thus, further investigation is needed in order to promote better food safety for consumers.

CONCLUSIONS

Rice is consumed worldwide and predictions indicate this will continue to increase. However, the health risks from the Al and heavy metal (Cr, Fe, Cu, Zn, As, Cd, and Pb) contents in cooked rice have led to serious concerns by consumers. This work used ICP-MS to quantify the contents of Al and heavy metals in raw/cooked rice samples and to assess potential non-carcinogenic and carcinogenic health risks from rice consumption. The results showed that of the tested metals, Al and Zn had the largest contents in raw/cooked rice, while commercial rice cookers, even with the use of acidic (pH =4) and basic (pH=10) water, did not leach substantial amounts of the relevant metals into the cooked rice. However, the Al and Pb contents in 0.3 kg of cooked rice consumed daily by a 60 kg person was greater than the recommended PTWI level issued the FAO/WHO. Furthermore, Pb, As, and Al
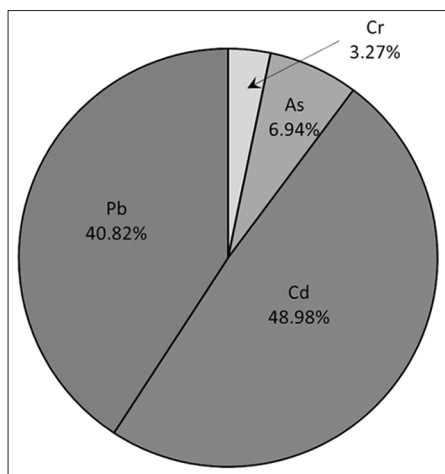
Fig 2. Total cancer risk (CRt) contributed by each metal of interest

contents posed potential non-carcinogenic risks as their *HQ* values were greater than 1, while the Cd, Pb, As, and Cr contents posed carcinogenic risks from rice consumption as their *CR* values were greater than 10^{-4}.

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Author's contributions

This work is part of the M.Sc. thesis of Anawat Rittirong (AR) advised by Kiadtisak Saenboonruang (KS). AR and KS have designed the study, conducted the experimental work, and analyzed data. KS wrote and revised the manuscript.

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