Heavy Metals in Sangyod Rice Samples Cultivated in Phatthalung, Thailand

Wannee Srinuttrakul[1,*], Vorapot Permnamtip[2] and Satoshi Yoshida[3]

Abstract

Sangyod rice is a traditional rice variety grown in Phatthalung province in the southern part of Thailand for more than a hundred years. In this study, inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the heavy metals (As, Cd, Cu, Mn and Zn) in Sangyod rice samples collected from six districts in Phatthalung. The highest mean concentrations of As and Mn were observed for rice samples from Si Banphot. Cd was highest in sample from Kong Ra and lowest in sample from Si Banphot. Bang Kaeo showed the highest content of Cu. Mueang had the greatest Zn concentration and lowest Cu level. The estimated daily intake of heavy metals resulting from rice consumption was 0.019–0.045 mg As day^{-1}, 0.003–0.013 mg Cd day^{-1}, 0.15–0.37 mg Cu day^{-1}, 2.94–3.75 mg Mn day^{-1} and 5.12–5.88 mg Zn day^{-1}, respectively. The percentage contribution to Provisional Tolerable Weekly Intake (PTWI) values of As and Cd for male was 12.9–30.3% and 4.7–18.4%, respectively, and for female was 15.6–36.7% and 5.7–22.3%, respectively. The obtained results showed all Sangyod rice samples from this study had the dietary intake of As and Cd lower than the PTWI values.

Keywords: Heavy metal, Sangyod rice, Dietary intake, Food safety

1. Introduction

Heavy metals in food are a great concern worldwide because of their toxicity. The quality of food can directly effect on human health. Some heavy metals are important nutrients for human but they are toxic at high concentrations such as copper (Cu), manganese (Mn) and zinc (Zn). Some heavy metals are toxic elements at very low level such as arsenic (As) and cadmium (Cd). A small quantity of Cu is a key component of redox enzymes and hemocyanin. It is involved in mitochondrial function, cellular metabolism, connective tissue formation, and the absorption, storage and metabolism of iron (Davis and Gatlin, 1996; McDowell, 1992).

[1] Research and Development Division, Thailand Institute of Nuclear Technology (Public Organization), Ongkharak, Nakhon Nayok, 26120, Thailand

[2] Nuclear Technology Service Center, Thailand Institute of Nuclear Technology (Public Organization), Ongkharak, Nakhon Nayok, 26120, Thailand

[3] Department of Management and Planning, National Institutes for Quantum and Radiological Science and Technology, Chiba, 263-8555, Japan

* Corresponding author(s), e-mail: neesrinut@yahoo.com

Mn functions as a required cofactor of several enzymes necessary for neuronal and glial cell function, as well as enzymes involved in neurotransmitter synthesis and metabolism (Erikson and Aschner, 2003; Hurley and Keen, 1987). Zn plays a crucial role in the development of brain (Takeda, 2001) and in maintaining the integrity of the blood brain barrier membrane (Pavlica and Gebhardt, 2010; Song *et al.*, 2008). Arsenic can cause cancer in internal organs (US EPA, 1993). Cd is a carcinogen causing bone diseases (US EPA, 1989).

Rice (*Oryza sativa*) is a major source of energy and nutrients and is a staple food in Thailand. There are many varieties of rice cultivated throughout the country of Thailand. Sangyod rice is the geographical indication product which it was originally cultivated only in Phatthalung province in the south of Thailand. Sangyod rice is well-known for its beautiful color; red, pink and white and the cooked rice is soft and scented. Sangyod rice has high nutrients such as iron, vitamin B, niacin and antioxidants (Department of Health, 2004; Srisawat *et al.*, 2010). The demand for Sangyod rice has increased and the price is higher than other local rice varieties.

For food safety, the accurate determination of heavy metals in rice is an important to evaluate the human dietary intake of heavy metals. Various techniques have been used for the heavy metal analysis in rice grain such as graphite furnace atomic absorption spectrometry (GFAAS) (Antoine *et al.*, 2012; Parengam *et al.*, 2010), instrumental neutron activation analysis (INAA) (Antoine *et al.*, 2012; Srinuttrakul and Busamongkol, 2010), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Ogiyama *et al*., 2008; Omar *et al*., 2015) and inductively coupled plasma mass spectrometry (ICP-MS) (Cheajesadagul *et al*., 2013; Pinto *et al*., 2016; Rahman *et al*., 2014). Among these techniques, ICP-MS is a useful technique with the advantage of simultaneous determination of multi-element, wide linear range, low detection limit and rapid analysis.

Therefore the objectives of this study were to determine the concentration of heavy metals (As, Cd, Cu, Mn and Zn) in Sangyod rice samples by ICP-MS and to evaluate the dietary intake of these metals from Sangyod rice consumption.

2. Materials and Methods

2.1 Sample collection and preparation

A total of 30 Sangyod rice samples were collected from the paddy fields throughout Phatthalung Province in February 2015. The sampling districts are Bang Kaeo, Khao Chaison, Kong Ra, Mueang, Pak Phayun and Si Banphot. Five rice samples were collected from different area of each district. About 2–3 kg of rice grains were harvested, dried, dehulled and polished to be the polished rice or white rice samples. All polished rice samples were ground by a high speed blender (1093 Cyclotec Sample Mill, Sweden) until fine powder passed completely through a 250 µm mesh sieve. The rice powders were dried in an electric oven at 60± 2°C until constant weight. Approximately 0.5 g of the rice powder was weighed into a polytetrafluoroethylene (PTFE) digestion vessel and was digested with 65% HNO_3 and 48% HF on a hot plate at 120°C. After digestion, the samples were evaporated to dryness and the residues were dissolved in 65% HNO_3 and 30% H_2O_2. The dissolved samples were evaporated to dryness and were diluted to 10 mL with 2% HNO_3. The standard reference material of rice flour (NIST 1568a) was also digested to check the procedure accuracy.

2.2 Sample analysis

The concentrations of heavy metals (As, Cd, Cu, Mn and Zn) in rice samples were determined by ICP-MS (Agilent 7900, Agilent Technologies, USA). The ICP-MS operating conditions for the determination of heavy metals were as follows: RF power, 1550 W; carrier gas flow rate, 0.8 L min^{-1}; makeup gas flow rate, 0.2 L min^{-1}; nebulizer pump, 0.1 rpm; nebulizer, Mira Mist; spray chamber, Scott type; Sampling cone and skimmer cone, Nickel. Indium (In) was used as an internal standard to compensate for any changes in analytical signals during the operation of ICP-MS. Standard solutions prepared from Agilent multi-element solution were used to create the standard calibration with minimum 5 points.

2.3 Estimated daily intake of heavy metals

The Estimated Daily Intake (EDI) of heavy metals resulting from rice consumption was calculated from the following formula:

$$EDI = C_{element} \times DC_{rice}$$

where $C_{element}$ is the mean value of each element in rice and DC_{rice} is the daily average rice consumption assumed to be 233 g $person^{-1}$ day^{-1} for Thai which is equivalent to yearly amount of about 85 kg per person (National Statistical Office and Office of Agricultural Economics of the Kingdom of Thailand, 2012).

2.4 Provisional tolerable weekly intake

The Provisional Tolerable Weekly Intake (PTWI) of toxic elements resulting from rice consumption was calculated from the following formula:

$$PTWI = C_{element} \times WC_{rice}/bw$$

where WC_{rice} is the average per capita weekly consumption of rice (1,631g) and bw is the individual's body weight assumed to be 69 kg for male and 57 kg for female of Thai (NECTEC, NSTDA, 2017).

3. Results and Discussion

3.1 Heavy metal concentrations in Sangyod rice samples

Thirty (30) Sangyod rice samples were analyzed for heavy metal concentrations (As, Cd, Cu, Mn, Zn) by ICP-MS presented in Table 1.

Table 1 Heavy metal concentrations in Sangyod rice samples (mg kg^{-1})

Cultivation district	As	Cd	Cu	Mn	Zn
Bang Kaeo	0.082±0.036	0.031±0.041	1.59±0.59	13.4±2.68	22.3±2.32
Khao Chaison	0.099±0.039	0.018±0.022	0.85±0.51	13.2±2.04	23.4±2.62
Kong Ra	0.084±0.020	0.055±0.036	1.40±0.37	12.6±2.74	22.0±1.31
Mueang	0.129±0.025	0.019±0.029	0.79±0.64	15.0±0.40	25.3±1.57
Pak Phayun	0.108±0.015	0.022±0.031	1.22±0.07	14.6±1.42	24.0±1.07
Si Banphot	0.192±0.073	0.014±0.023	1.11±0.32	16.1±1.97	24.0±3.24

3.1.1 Arsenic

The range concentrations of As in Sangyod rice samples cultivated in six districts of Phatthalung were 0.022–0.117 mg kg^{-1} (Bang Kaeo), 0.066–0.163 mg kg^{-1} (Khao Chaison), 0.061–0.117 mg kg^{-1} (Kong Ra), 0.112–0.173 mg kg^{-1} (Mueang), 0.094–0.133 mg kg^{-1} (Pak Phayun), and 0.065–0.248 mg kg^{-1} (Si Banphot), respectively. The highest mean concentration of As (0.192±0.073 mg kg^{-1}) was observed for rice samples from Si Banphot. Whereas Rice samples from Bang Kaeo showed the lowest mean content of As (0.082±0.036 mg kg^{-1}). Arsenic is a toxic heavy metal that is occurred naturally and contaminated in the environment by human activities (Hang *et al.*, 2009). A draft maximum limit of inorganic arsenic for polished rice resulted from Codex (FAO, 2014) meeting was 0.2 mg kg^{-1}. The concentration of As observed from this study (0.022–0.248 mg kg^{-1}) was the total arsenic. EFSA (EFSA, 2014) reported that inorganic arsenic represents approximately 70% of the total arsenic. Therefore the inorganic As concentration of Sangyod rice samples calculated based on EFSA report was 0.016–0.174 mg kg^{-1}. All studied rice samples showed the inorganic arsenic was lower than the maximum limit.

3.1.2 Cadmium

The Cd content in Sangyod rice samples were <0.0013–0.079 mg kg^{-1} (Bang Kaeo), 0.003–0.054 mg kg^{-1} (Khao Chaison), 0.009–0.108 mg kg^{-1} (Kong Ra), 0.002–0.071 mg kg^{-1} (Mueang), <0.0013–0.076 mg kg^{-1} (Pak Phayun), and 0.003–0.055 mg kg^{-1} (Si Banphot), respectively. The highest mean concentration of Cd was found for Kong Ra with 0.055±0.036 mg kg^{-1}. Cd is a toxic element. Codex (Codex, 1995) has established a limit of Cd in polished rice of 0.4 mg kg^{-1}. All Sangyod rice samples from this study had Cd lower than the limit data.

3.1.3 Copper

The range of Cu level in Sangyod rice samples was 1.09–2.29 mg kg^{-1} (Bang Kaeo), 0.44–1.68 mg kg^{-1} (Khao Chaison), 0.85–1.80 mg kg^{-1} (Kong Ra), 0.057–1.82 mg kg^{-1} (Mueang), 1.11–1.30 mg kg^{-1} (Pak Phayun), and 0.82–1.50 mg kg^{-1} (Si Banphot), respectively. Sangyod rice samples from Bang Kaeo had the highest mean value (1.59±0.59 mg kg^{-1}) while rice samples from Mueang showed the lowest level with 0.79±0.64 mg kg^{-1}.

3.1.4 Manganese

The concentration of Mn in Sangyod rice samples was 10.58-16.39 mg kg^{-1} (Bang Kaeo), 11.5–16.5 mg kg^{-1} (Khao Chaison), 8.73–15.8 mg kg^{-1} (Kong Ra), 14.4–15.4 mg kg^{-1} (Mueang), 13.1–16.7 mg kg^{-1} (Pak Phayun), and 13.4–19.0 mg kg^{-1} (Si Banphot), respectively. Sangyod rice samples from Si Banphot had the greatest mean content of 16.1±1.97 mg kg^{-1}, whereas rice samples from Kong Ra had the lowest mean level (12.6±2.74 mg kg^{-1}).

3.1.5 Zinc

The amount of Zn in Sangyod rice samples was 19.5-25.1 mg kg^{-1} (Bang Kaeo), 20.6–26.9 mg kg^{-1} (Khao Chaison), 20.6–23.5 mg kg^{-1} (Kong Ra), 24.0–27.7 mg kg^{-1} (Mueang), 22.6–24.9 mg kg^{-1} (Pak Phayun), and 21.2–29.3 mg kg^{-1} (Si Banphot), respectively. The highest mean concentration (25.3±1.57 mg kg^{-1}) was observed in rice samples from Mueang and the lowest content (22.0±1.31mg kg^{-1}) was found in rice samples from Kong Ra.

3.2 Dietary intake of heavy metals

The Estimated Daily Intake (EDI) of heavy metals from rice consumption was evaluated and given in Table 2 and Table 3. The results of heavy metals which are essential elements were also compared with Recommended Daily Intake (RDI) (HHS, 2010) summarized in Table 2.

The mean daily intake of Cu ranged from 0.18 to 0.37 mg for Sangyod rice samples. Cu is an essential nutrient for humans with RDI of 0.9 mg day^{-1}. Sangyod rice appears to be a significant source of Cu with providing 20–41% of the RDI for both males and females.

The mean daily intake of Mn from Sangyod rice samples was 2.94–3.75 mg, which it was lower than the tolerable upper limit of Mn (11 mg day^{-1}) (Institute of Medicine (US), 2001). Mn is an essential element for humans with a recommended daily intake ranging from 1.8 to 2.3 mg. Sangyod rice is an important source of Mn with the intake more than 120% of the RDI.

The mean daily intake of Zn varied from 5.12-5.88 for Sangyod rice samples. Zn is an essential element for humans with RDI of 11 and 8 mg day^{-1} for males and females, respectively. Sangyod rice samples contributed 47–53% of the RDI for Zn for males and provided 64–74% of the RDI for Zn for females, respectively. Therefore Sangyod rice is a major source of Zn. The Zn deficiency has been found in the low income countries. This finding indicated that Zn deficiency is not a concern in Sangyod rice.

Table 2 Estimated daily intake (EDI) of heavy metals from Sangyod rice according to the cultivation area

Elements	**Mean Daily Intake (mg day^{-1})**	**RDI (mg day^{-1}) (Male)** (HHS, 2010)	**RDI (mg day^{-1}) (Female)** (HHS, 2010)	**% of RDI (Male)**	**% of RDI (Female)**
Si Banphot					
Cu	0.26	0.9	0.9	29	29
Mn	3.75	2.3	1.8	163	209
Zn	5.59	11	8	51	70
Mueang					
Cu	0.18	0.9	0.9	20	20
Mn	3.50	2.3	1.8	152	195
Zn	5.88	11	8	53	74
Kong Ra					
Cu	0.32	0.9	0.9	36	36
Mn	2.94	2.3	1.8	128	163
Zn	5.12	11	8	47	64
Khao Chaison					
Cu	0.20	0.9	0.9	22	22
Mn	3.08	2.3	1.8	134	171
Zn	5.45	11	8	50	68
Bang Kaeo					
Cu	0.37	0.9	0.9	41	41
Mn	3.12	2.3	1.8	136	173
Zn	5.20	11	8	47	65
Pak Phayun					
Cu	0.28	0.9	0.9	32	32
Mn	3.40	2.3	1.8	148	189
Zn	5.60	11	8	51	70

Table 3 Provisional Tolerable Weekly Intake (PTWI) of toxic elements by Thai consumer

Elements	Mean Daily Intake (mg day^{-1})	PTWI (mg kg^{-1} bw) (JECFA, 2011)	% of the established PTWI	
			Male	Female
Si Banphot				
As	0.045	0.015	30.3	36.7
Cd	0.003	0.007	4.7	5.7
Mueang				
As	0.030	0.015	20.4	24.7
Cd	0.005	0.007	6.6	8.0
Kong Ra				
As	0.020	0.015	13.3	16.1
Cd	0.013	0.007	18.4	22.3
Khao Chaison				
As	0.023	0.015	15.7	19.0
Cd	0.004	0.007	6.2	7.5
Bang Kaeo				
As	0.019	0.015	12.9	15.6
Cd	0.007	0.007	10.5	12.7
Pak Phayun				
As	0.025	0.015	17.1	20.7
Cd	0.005	0.007	7.4	9.0

3.3 Provisional tolerable weekly intake

The Provisional Tolerable Weekly Intakes (PTWIs) of toxic elements such as As and Cd,, from Sanyod rice consumption was investigated. The obtained PTWI values were compared with the PTWI values established by the Joint FAO/WHO Committee on Contaminants in Foods (JECFA, 2011), shown in Table 3.

The estimated contribution from As ranged from 12.9–36.7% of PTWI. The daily intake of As was highest in rice samples from Si Banphot with 30.3% and 36.7% of the PTWI for males and females, respectively. The daily intake of As from this study (Table 3) was calculated from the total arsenic. Thus the daily intake of inorganic arsenic from rice samples of Si Banphot was 21.2% and 25.7% of the PTWI for males and females, respectively. Although a little bit high value of PTWI was observed for rice samples from Si Banphot, none of Sangyod rice samples from this study had the dietary intake of As higher than the PTWI.

The daily intake of Cd was 4.7–22.3% of PTWI. The greatest contribution from Cd was 18.4% of the PTWI for males and 22.3% for females found for rice samples from Kong Ra. All studied samples did not significantly contribute for the PTWI of Cd.

All Sangyod rice samples from this study had the dietary intake of As and Cd lower than the PTWI values. Therefore, the studied Sangyod rice samples are safe for consumption.

4. Conclusion

Thirty Sangyod rice samples cultivated in Phatthalung of the southern part of Thailand were analyzed for their heavy metals (As, Cd, Cu, Mn, Zn) by ICP-MS. The results indicated that Sangyod rice can be served as an important dietary source of Mn, Zn and Cu. Furthermore, Sangyod rice samples used in this study are safe for consumption.

Acknowledgements

We would like to thank the staff of Agricultural Extension Office for their assistance in cooperation with the farmers. We thank the farmers for their rice samples. Ms.Arporn Busamongkol, Mr.Saman Photong and Ms.Tongmueang Suksawasdi are acknowledged for their help in sample collection.

References

Antoine, J.M.R., Fung, L.A.H., Grant, C.N., Dennis, H.T. and Lalor, G.C. 2012, Dietary intake of minerals and trace elements in rice on the Jamaican market. Journal of Food Composition and Analysis. 26:111–121.

Cheajesadagul, P., Arnaudguilhem, C., Shiowatana, J., Siripinyanond, A. and Szpunar, J. 2013. Discrimination of geographical origin of rice based on multi-element fingerprinting by high resolution inductively coupled plasma mass spectrometry. Food Chemistry. 141:3504–3509.

Codex. 1995. Codex general standard for contaminants and toxins in food and feed. Codex Alimentarius Commission. Rome, Italy, (Codex Standard 193–1995).

Davis, D.A., Gatlin and D.M. 1996. Dietary mineral requirements of fish and marine crustaceans. Review in Fisheries Science. 4:75–99.

Department of Health. 2004. Nutrition analysis of Sanyod Phatthalung rice. Department of Health, Ministry of Public Health, Thailand.

EFSA. 2014. Dietary exposure to inorganic arsenic in the European population. EFSA Journal. 12(3):3597.

Erikson, K.M. and Aschner, M. 2003. Manganese neurotoxicity and glutamate–GABA interaction. Neurochemistry International. 43:475–480.

FAO-Food and Agriculture Organization of the United Nations. 2014. Report of the Eight Session of the Codex Committee on Contaminants in Foods.

Hang, X., Wang, H., Zhou, J., Ma, C., Du, C. and Chen, X. 2009. Risk assessment of potentially toxic element pollution in soils and rice (Oryza sativa) in a typical area of the Yangtze River Delta. Environmental Pollution. 157:2542–2549.

HHS. 2010. United States Department of Agriculture/United States Department of Health and Human Services, Dietary Guidelines for Americans 2010. Washington, DC, USA.

Hurley, L.S. and Keen, C.L. 1987. Manganese. Underwood, E. and Mertz, W. (Eds.). In Trace elements in human health and animal nutrition (pp.185-223). Academic Press, New York.

Institute of Medicine (US). 2001. Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc. National Academy Press. Washington DC.

JECFA. 2011. Joint FAO/WHO food standards programme Codex Committee on contaminants in foods: Working document for information and use in discussions related to contaminants and toxins in the GSCTFF.

McDowell, L.R. 1992. Minerals in Animal and Human Nutrition. Academic Press Inc, CA, USA.

National Statistical Office and Office of Agricultural Economics of the Kingdom of Thailand. 2012. Food insecurity assessment at national and subnational levels in Thailand, 2011. Bangkok, Thailand.

NECTEC, NSTDA. SizeThai (Online). Avaiable: http://www.sizethailand.org/region_all.html.

Ogiyama, S., Tagami, K. and Uchida, S. 2008. The concentration and distribution of essential elements in brown rice associated with the polishing rate: Use of ICP-AES and Micro-PIXE. Nuclear Instruments and Methods in Physics Research B. 266: 3625–3632.

Omar, N.A., Praveena, S.M., Aris, A.Z. and Hashim, Z. 2015. Health Risk Assessment using in vitro digestion model in assessing bioavailability of heavy metal in rice: A preliminary study. Food Chemistry. 188:46–50.

Parengam, M., Judprasong, K., Srianujata, S., Jittinandana, S., Laoharojanaphand, S. and Busamongkol, A. 2010. Study of nutrients and toxic minerals in rice and legumes by instrumental neutron activation analysis and graphite furnace atomic absorption spectrophotometry. Journal of Food Composition and Analysis. 23:340–345.

Pavlica, S. and Gebhardt, R. 2010. Comparison of uptake and neuroprotective potential of seven zinc-salts. Neurochemistry International. 56:84–93.

Pinto, E., Almeida, A. and Ferreira, I. 2016. Essential and non-essential/toxic elements in rice available in the Portuguese and Spanish markets. Journal of Food Composition and Analysis. 48:81–87.

Rahman, M.A., Rahman, M.M., Reichman, S.M., Lim, R.P. and Naidu, R. 2014. Heavy metals in Australian grown and imported rice and vegetables on sale in Australia: Health hazard. Ecotoxicology and Environmental Safety. 100:53–60.

Song, Y., Xue, Y., Liu, X., Wang, P. and Liu, L. 2008. Effects of acute exposure to aluminum on blood-brain barrier and the protection of zinc. Neuroscience Letters. 445:42–46.

Srinuttrakul, W. and Busamongkol, A. 2014. Elemental Analysis of Brown Rice by Inductively Coupled Plasma Atomic Emission Spectrometry and Instrumental Neutron Activation Analysis. Energy Procedia. 56:85–91.

Srisawat, U., Panunto, W., Kaendee, N., Tanuchit, S., Itharat, A., Lerdvuthisopon, N. and Hansakul. P. 2010. Determination of phenolic compounds, flavonoids, and antioxidant activities in water extracts of Thai red and white rice cultivars. Journal of the Medical Association of Thailand. 93:S83–S91.

Takeda, A. 2001. Zinc homeostasis and functions of zinc in the brain. Biometals. 14:343–351.

United States Environmental Protection Agency (US EPA). 1993. Arsenic, Inorganic; Environmental Protection Agency, Integrated Risk Information System: Washington, DC, USA.

United States Environmental Protection Agency (US EPA). 1989. Cadmium; Environmental Protection Agency, Integrated Risk Information System: Washington, DC, USA.