

# Evaluation of Toxic Elements in Thai Rice Samples

W. Srinuttrakul, V. Permmamtip

**Abstract**—Toxic elements in rice samples are great concern in Thailand because rice (*Oryza sativa*) is a staple food for Thai people. Furthermore, rice is an economic crop of Thailand for export. In this study, the concentrations of arsenic (As), cadmium (Cd) and lead (Pb) in rice samples collected from the paddy fields in the northern, northeastern and southern regions of Thailand were determined by inductively coupled plasma mass spectrometry. The mean concentrations of As, Cd and Pb in 55 rice samples were  $0.112 \pm 0.056$ ,  $0.029 \pm 0.037$  and  $0.031 \pm 0.033$  mg kg<sup>-1</sup>, respectively. All rice samples showed As, Cd and Pb lower than the limit data of Codex. The estimated daily intakes (EDIs) of As, Cd, and Pb from rice consumption were  $0.026 \pm 0.013$ ,  $0.007 \pm 0.009$  and  $0.007 \pm 0.008$  mg day<sup>-1</sup>, respectively. The percentage contribution to Provisional Tolerable Weekly Intake (PTWI) values of As, Cd and Pb for Thai male (body weight of 69 kg) was 17.6%, 9.7%, and 2.9%, respectively, and for Thai female (body weight of 57 kg) was 21.3%, 11.7% and 3.5%, respectively. The findings indicated that all studied rice samples are safe for consumption.

**Keywords**—Arsenic, cadmium, ICP-MS, lead, rice.

## I. INTRODUCTION

THE increasing of heavy metal levels in the environment has been a great concern worldwide because of their toxicity. Heavy metals such as As, Cd and Pb are classified as toxic elements. These toxic elements have been widely found in the environment including soil, water and air, because they are naturally occurring substances and contamination from human activity [1]-[4]. Toxic elements cannot be degraded therefore they can accumulate in the food chain, causing a serious problem to human health. Toxic elements in the environment can enter to agricultural crops via root uptake or aerial contamination. The intake of agricultural crops or foodstuffs contaminated with toxic elements is the main exposure pathway to human.

The intake of toxic elements can cause the adverse effect to human health. As can cause cancer in liver, kidney, lung, bladder and skin [5]. Cd is a carcinogen and nephrotoxin causing renal tubular and skeletal damages [6]. Pb can damage the brain and nervous system, causing neurological disorders [7]. Hence, it is important to control the levels of these toxic elements in agricultural crops or foodstuffs in order to protect human health.

Rice (*Oryza sativa* L.) is a staple food for Thai and is an

important economic crop of Thailand for export. Thus, rice is the main route of toxic elements exposure to human, causing a high potential health risk. The published data of toxic elements in Thai rice are limited. Parengam et al. investigated the nutrients and toxic minerals in Thai rice by instrumental neutron activation analysis and graphite furnace atomic absorption spectrophotometry [8]. Four varieties of rice were bought from the markets in Thailand. Cheajesadagul et al. studied the multi-elements including toxic elements in Thai jasmine rice and foreign rice by high resolution inductively coupled plasma mass spectrometry using for discrimination of rice origin [9]. 30 Thai jasmine white rice samples were collected from the northeastern, northern and central regions of Thailand. Although the level of toxic elements from the literature reports is below the permissible level, it is necessary to study more because of the increasing trend of toxic elements accumulated in the environment especially in the paddy field. The rice samples collected directly from the paddy field are very useful to get the real information of toxic element concentration.

The purpose of this study was to determine the concentrations of As, Cd and Pb in Thai rice samples collected from the different cultivation regions (north, northeast and south) of Thailand by inductively coupled plasma mass spectrometry (ICP-MS). The estimated daily intake (EDI) and PTWI of As, Cd, and Pb resulting from rice consumption were also investigated.

## II. MATERIALS AND METHODS

### A. Reagents and Standards

Nitric acid 65% (suprapure analytical grade), hydrofluoric acid 48% (analytical grade) and hydrogen peroxide 30% (analytical grade) were purchased from Merck (Darmstadt, Germany). All solutions were prepared using ultrapure water ( $>18$  M $\Omega$  cm) obtained with a Milli-Q (Millipore, Billerica, MA, USA) water purification system. The standard solution was purchased from Agilent Technologies (New Haven, CT, USA). The standard reference material was rice flour (NIST 1568a) from National Institute of Standards and Technology (NIST; MD, USA).

### B. Sample Collection and Preparation

Rice grains (2-3 kg) were harvested from the paddy field in the northern ( $n = 10$ ), northeastern ( $n = 25$ ) and southern ( $n = 20$ ) regions in 2014-2016. The rice samples were air-dried at room temperature. All samples were dehulled to be polished rice or white rice and were ground by a high speed blender (1093 Cyclotec Sample Mill, Sweden) to obtain fine powder (250  $\mu$ m). The rice powders were dried again in an oven at  $60 \pm 2$  °C until constant weight, kept in polyethylene containers

W. Srinuttrakul is with the Thailand Institute of Nuclear Technology (Public Organization), Ongkharak, Nakhon Nayok 26120 Thailand (corresponding author, phone: +66-37-392-901; fax: +66-37-392-913; e-mail: neesrinut@yahoo.com).

V. Permmamtip is with the Thailand Institute of Nuclear Technology (Public Organization), Ongkharak, Nakhon Nayok 26120 Thailand (e-mail: vorapotp@tint.or.th).

This work has been financially supported by the International Atomic Energy Agency (Research Contract No. 16523).

and stored in a desiccator until analysis.

All powdered rice samples (0.5 g) were digested in PTFE vessels with 10 mL of 65% HNO<sub>3</sub> and 4 mL of 48% HF on a hot plate at 140 °C for 5 h. After digestion, the samples were evaporated to dryness and the residues were dissolved in 65% HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub>. After drying, the residues were dissolved with 2% HNO<sub>3</sub> as reported by Srinuttrakul et al. [10]. Sample digestions were done in triplicate. The standard reference material of rice flour (NIST 1568a) was used to check the procedure accuracy.

#### C. Determination of As, Cd and Pb by ICP-MS

The concentrations of As, Cd and Pb in rice samples were determined by ICP-MS (Agilent 7900, Agilent Technologies, USA). The ICP-MS instrument operational parameters were as follow: RF power, 1550 W; carrier gas flow, 0.8 L min<sup>-1</sup>; makeup gas flow, 0.2 L min<sup>-1</sup>; nebulizer pump, 0.1 rps. The following elemental isotopes m/z ratios were monitored for analytical determinations: <sup>75</sup>As, <sup>111</sup>Cd and <sup>207</sup>Pb. Indium (In) and Bismuth (Bi) were used as internal standard to compensate for changes in analytical signals during the operation. The instrument was tuned daily for maximum signal sensitivity and stability as well as for low oxides and doubly charged ion formation using the tuning solution for ICP-MS 7500cs (Agilent Technologies, USA; 1 µg L<sup>-1</sup> of Ce, Co, Li, Mg, Tl and Y in 2% HNO<sub>3</sub>). Limits of detection (LOD) were estimated from 10 measurements of the blank solution (2%v/v HNO<sub>3</sub>). Standard solutions were prepared from Agilent multi-element solution and used to get calibration curves at least 5 points.

#### D. Estimated Daily Intake of Elements

The EDI of toxic elements resulting from rice consumption was calculated using (1),

$$EDI = C_{\text{element}} \times DC_{\text{rice}} \quad (1)$$

where  $C_{\text{element}}$  is the mean value of each element in rice, and  $DC_{\text{rice}}$  is the daily average rice consumption assumed to be 233 g/person/day for Thai which is equivalent to yearly amount of about 85 kg per person [11].

#### E. Provisional Tolerable Weekly Intake

The PTWI of toxic elements resulting from rice consumption was calculated using (2),

$$PTWI = \frac{C_{\text{element}} \times WC_{\text{rice}}}{bw} \quad (2)$$

where  $WC_{\text{rice}}$  is the average per capita weekly consumption of rice (1,631 g) and  $bw$  is the individual's body weight assumed to be 69 kg for Thai male and 57 kg for Thai female [12].

#### F. Statistical Analysis

The statistical analysis of Microsoft Office Excel 2007 was used to calculate the mean, and standard deviation (SD). The difference between the means of two data sets was evaluated using the Student's *t*-test at the 95% confidence interval (*t*-test;  $p < 0.05$ ).

### III. RESULTS AND DISCUSSION

#### A. Method Validation

For quality control purpose, the standard reference material of rice flour (NIST 1568a) was analyzed under the same condition as for the sample. Good agreements between the certified and measured values were observed for the standard reference material (Table I). Error of observed values for As and Cd was less than 5% of the certified value.

TABLE I  
MEASURED VALUE OF RICE FLOUR (NIST 1568A) AND LIMIT OF DETECTION (LOD) BY ICP-MS

Element	As	Cd	Pb
Certified value (mg kg <sup>-1</sup> )	0.290 ± 0.030	0.022 ± 0.002	<0.010
Measured value (mg kg <sup>-1</sup> )	0.291 ± 0.014	0.021 ± 0.002	<0.005
Recovery (%)	100.3 ± 4.8	95.5 ± 9.1	Not detectable
LOD (mg kg <sup>-1</sup> )	0.003	0.0013	0.005

#### B. Concentrations of As, Cd and Pb in Thai Rice Samples

The concentrations of As, Cd and Pb in 55 Thai rice samples analyzed by ICP-MS were given in Table II. The order of elemental concentration was As > Pb > Cd. The concentration ranges of As, Cd and Pb were 0.022-0.272, 0.002-0.177 and <0.005-0.137 mg kg<sup>-1</sup>, respectively. The mean values of As, Cd and Pb were 0.112±0.056, 0.029±0.037, and 0.031±0.033 mg kg<sup>-1</sup>, respectively. The max./min. concentration ratios of As, Cd and Pb varied from 12 to 86. The relative standard deviation (RSD) in the concentration of the toxic elements in all studied samples was 50-108. The high value of the max./min. ratio and RSD was observed for Cd. The result indicated that the concentration of Cd in rice samples varied widely.

The concentrations of As, Cd and Pb in Thai rice samples from the present study were compared with the previous data reported by Parengam et al. [8] and Cheajesadagul et al. [9]. The obtained values were well within reported ranges, except for Cd, which showed higher level than the previous study [8] (0.103 ± 0.02 [8] and 0.092-0.161 [9] mg kg<sup>-1</sup> for As, 0.013 ± 0.005 [8] and 0.004-0.017 [9] mg kg<sup>-1</sup> for Cd and < 0.01 [8] and LOD-0.512 [9] mg kg<sup>-1</sup> for Pb).

TABLE II  
SUMMARY STATISTICS OF TOXIC ELEMENTS IN THAI RICE SAMPLES

Value	As (mg kg <sup>-1</sup> )	Cd (mg kg <sup>-1</sup> )	Pb (mg kg <sup>-1</sup> )
Number of sample	55	55	55
Mean	0.112	0.029	0.031
SD	0.056	0.037	0.033
%RSD	50	128	108
Minimum	0.022	0.002	<0.005
Maximum	0.272	0.177	0.137
Max./Min.	12	86	27

The obtained results from this study were compared with the data of rice from different sources shown in Table III. Thai rice had As content higher than Japanese, Brazilian and Jamaican rice. The highest As was found in Spanish rice. The Cd level in Thai rice was similar to the other rice sources,

except for Brazilian rice. The Pb concentration in Thai rice was higher than for the others except for Spanish rice. The different concentration of elements in rice samples was attributed to the topography, soil property and condition, and application of fertilizer and pesticide to agricultural area reported by Kelly et al. [18].

TABLE III  
COMPARISONS OF TOXIC ELEMENT CONCENTRATIONS IN RICE OF DIFFERENT SOURCES

Sample	As (mg kg <sup>-1</sup> )	Cd (mg kg <sup>-1</sup> )	Pb (mg kg <sup>-1</sup> )
Thai rice (this study)	0.112 ± 0.056	0.028 ± 0.037	0.031 ± 0.033
Japanese rice (n=20) [13]	0.085 ± 0.029	0.030 ± 0.033	0.011 ± 0.028
Japanese rice (n=37) [14]	0.057 <sup>a</sup>	0.060 <sup>a</sup>	0.007 <sup>a</sup>
Spanish rice-Valencia (n=52) [15]	0.5 <sup>a</sup>	0.02 <sup>a</sup>	0.4 <sup>a</sup>
Brazilian rice (n=5) [16]	0.012 <sup>a</sup>	0.0048 <sup>a</sup>	0.005 <sup>a</sup>
Jamaican rice (n=1) [17]	0.05 <sup>a</sup>	0.066 <sup>a</sup>	No data

<sup>a</sup>Mean

### C. Comparison of Toxic Elements among Cultivation Regions

#### 1) Arsenic

The As concentration in rice sample cultivated in the northern, northeastern and southern regions (Fig. 1) ranged from 0.061-0.089, 0.032-0.272 and 0.022-0.225 mg kg<sup>-1</sup>, respectively, with the mean of 0.075, 0.125, and 0.114 mg kg<sup>-1</sup>, respectively. Significant difference (*t* test; *p* < 0.05) of mean as content was found between rice samples from the northern and southern regions. A draft maximum limit of inorganic As for polished rice resulted from Codex [19] meeting was 0.2 mg kg<sup>-1</sup>. The concentration of as observed from this study (0.022-0.272 mg kg<sup>-1</sup>) was the total As. EFSA [20] reported that inorganic As represents approximately 70% of the total As. Therefore, the inorganic as concentration of Thai rice samples calculated based on EFSA report was 0.016-0.190 mg kg<sup>-1</sup>. All rice samples showed the inorganic As was below the maximum limit set by the Codex.

#### 2) Cadmium

The Cd content in Thai rice samples from the northern, northeastern and southern regions (Fig. 2) varied from 0.006-0.177, 0.002-0.065 and 0.002-0.079 mg kg<sup>-1</sup>, respectively. The highest mean concentration of Cd was found for the northern region with 0.075 mg kg<sup>-1</sup>. The mean Cd concentration in rice samples from the northern region was significant difference (*t* test; *p* < 0.05) from the northeastern and southern regions. Codex [21] has established a limit of Cd in polished rice of 0.4 mg kg<sup>-1</sup>. All rice samples from the present study had Cd lower than the limit data.

#### 3) Lead

The range of Pb level in Thai rice samples from the northern, northeastern and southern regions (Fig. 3) was <0.005-0.046, <0.005-0.112 and <0.005-0.137 mg kg<sup>-1</sup>, respectively. The highest mean value (0.055 mg kg<sup>-1</sup>) was observed in rice sample from the southern region and lowest level (0.026 mg kg<sup>-1</sup>) was found for the northern area. There was no significant difference of Pb content among regions.

The concentration of Pb in Thai rice samples from this work was below the limit of Pb in polished rice established by Codex (0.2 mg kg<sup>-1</sup>) [21].

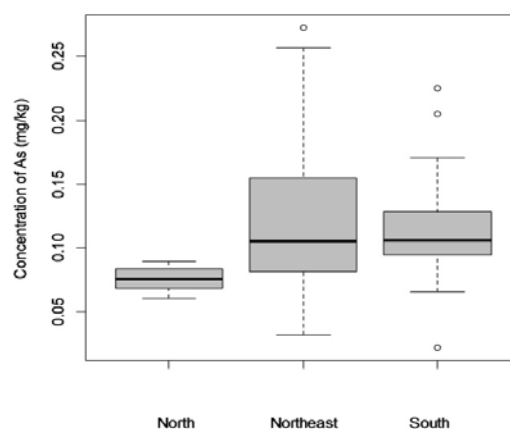


Fig. 1 Boxplot showing variation of as concentrations in Thai rice samples according to the cultivation region

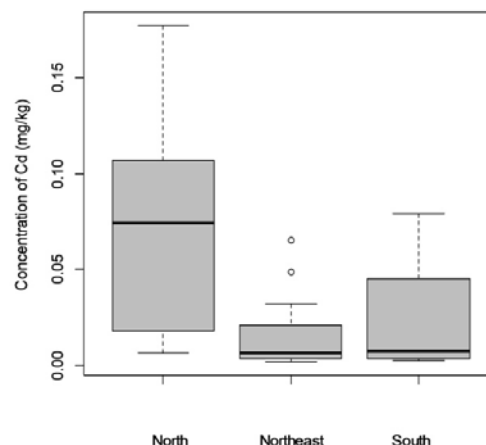


Fig. 2 Boxplot showing variation of Cd concentrations in Thai rice samples according to the cultivation region

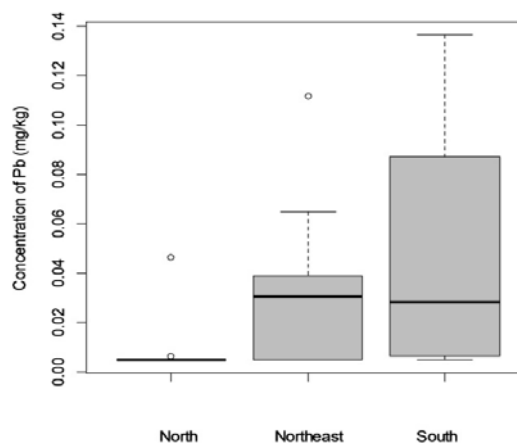


Fig. 3 Boxplot showing variation of Pb concentrations in Thai rice samples according to the cultivation region

#### D. Estimated Daily Intake of Elements

The EDI of toxic elements from rice consumption was summarized in Table IV. From the present study, the EDIs of As, Cd, and Pb from rice consumption were  $0.026 \pm 0.013$ ,  $0.007 \pm 0.009$  and  $0.007 \pm 0.008$  mg day<sup>-1</sup>, respectively.

#### E. Provisional Tolerable Weekly Intake

The PTWI of toxic elements from rice consumption was evaluated. The obtained PTWI values were compared with the PTWI values established by the Joint FAO/WHO Committee on Contaminants in Foods [22], as shown in Table IV. The daily intake of As from rice is highest with 17.6% of the PTWI for males and 21.3% of the PTWI for females. The greatest contribution from Cd is 9.7% of the PTWI for males and 11.7% for females. The estimated contribution from Pb is highest with 2.9% of the PTWI for males and 3.5% of the PTWI for females. From the present results, rice does not significantly contribute for the PTWI of As, Cd and Pb.

TABLE IV  
DAILY INTAKE ESTIMATED FOR TOXIC ELEMENTS FROM THAI RICE SAMPLES

Element	As	Cd	Pb
Mean (mg kg <sup>-1</sup> )	0.112	0.029	0.031
Estimated dairy intake (mg day <sup>-1</sup> )	0.026	0.007	0.007
PTWI (mg kg <sup>-1</sup> bw) [22]	0.015	0.007	0.025
% of PTWI (Male)	17.6	9.7	2.9
% of PTWI (Female)	21.3	11.7	3.5

#### IV. CONCLUSION

ICP-MS is a powerful technique to determine toxic elements (As, Cd and Pb) in rice samples with the rapid, very low detection limit and multi-element analysis. The concentrations of As, Cd and Pb in Thai rice samples collected from the northern, northeastern and southern regions of Thailand were analyzed by ICP-MS. The results indicated that all studied Thai rice samples are safe for consumption. The obtained data from this study might be useful for reliable estimation of dietary intake of toxic elements from Thai rice.

#### ACKNOWLEDGMENT

We would like to thank the staff of Agricultural Extension Office for their assistance in cooperation with the farmers. We are grateful to the farmers for their kind support of rice samples. A. Busamongkol, S. Photong and T. Suksawasdi are acknowledged for their help in sample collection.

#### REFERENCES

- [1] X. Hang, H. Wang, J. Zhou, C. Ma, C. Du, X. Chen, "Risk assessment of potentially toxic element pollution in soils and rice (*Oryza sativa*) in a typical area of the Yangtze River Delta", *Environ. Pollut.* vol. 157, pp. 2542-2549, 2009.
- [2] M. Nadimi-Goki, M. Wahsha, C. Bini, T. Kato, G. Vianello, L. V. Antisari, "Assessment of total soil and plant elements in rice-based production systems in NE Italy.", *J. Geochem. Explor.* vol. 147, pp. 200-214, 2014.
- [3] L. Ma, L. Wang, Y. Jia, Z. Yang, "Arsenic speciation in locally grown rice grains from Hunan Province, China: Spatial distribution and potential health risk", *Sci. Total Environ.* vol. 557-558, pp. 438-444, 2016.

- [4] A. Shrivastava, A. Barla, S. Singh, S. Mandraha, S. Bose, "Arsenic contamination in agricultural soils of Bengal deltaic region of West Bengal and its higher assimilation in monsoon rice" *J. Hazard. Mater.* vol. 324, pp. 526-534, 2017.
- [5] United States Environmental Protection Agency (US EPA). Arsenic, Inorganic; Environmental Protection Agency, Integrated Risk Information System: Washington, DC, USA, 1993; CASRN 7440-38-2.
- [6] United States Environmental Protection Agency (US EPA). Cadmium; Environmental Protection Agency, Integrated Risk Information System: Washington, DC, USA, 1989; CASRN 7440-43-9.
- [7] United States Environmental Protection Agency (US EPA). Lead and Compounds (Inorganic); Environmental Protection Agency, Integrated Risk Information System: Washington, DC, USA, 2004; CASRN 7439-92-1.
- [8] M. Parengam, K. Judprasong, S. Srianujata, S. Jittinandana, S. Laoharojanaphand, A. Busamongkol, "Study of nutrients and toxic minerals in rice and legumes by instrumental neutron activation analysis and graphite furnace atomic absorption spectrophotometry", *J. Food Compos. Anal.* vol. 23, pp. 340-345, 2010.
- [9] P. Cheajesadagul, C. Arnaudguilhem, J. Shiowatana, A. Siripinyanond, J. Szpunar, "Discrimination of geographical origin of rice based on multi-element fingerprinting by high resolution inductively coupled plasma mass spectrometry.", *Food Chem.* vol. 141, pp. 3504-3509, 2013.
- [10] W. Srinuttrakul, A. Busamongkol, "Elemental analysis of brown rice by inductively coupled plasma atomic emission spectrometry and instrumental neutron activation analysis", *Enrgy. Proced.* vol. 56, pp. 85-91, 2014.
- [11] 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.
- [12] [http://www.sizethailand.org/region\\_all.html](http://www.sizethailand.org/region_all.html) (accessed August 1, 2017).
- [13] H. Tsukada, H. Hasegawa, A. Takeda, S. Hisamatsu, "Concentrations of major and trace elements in polished rice and paddy soils collected in Aomori, Japan". *J. Radioanal. Nucl. Ch.* vol. 273, pp. 199-203, 2007.
- [14] S. Uchida, K. Tagami, I. Hirai, "Soil-to-plant transfer factors of stable elements and occurring radionuclides: (2) Rice collected in Japan", *J. Nucl. Sci. Technol.* Vol. 44, pp. 779-790, May 2007.
- [15] A. González, S. Armenta, M. de la Guardia, "Geographical traceability of "Arròs de Valencia" rice grain based on mineral element composition", *Food Chem.* vol. 126, pp. 1254-1260, 2011.
- [16] E. P. Nardi, F. S. Evangelista, L. Tormen, T. D. Saint-Pierre, A. J. Curtius, S. S. de Souza, F. B. Jr. "The use of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples", *Food Chem.* vol. 112, pp. 727-732, 2009.
- [17] J. M. R. Antoine, L. A. Hoo Fung, C. N. Grant, H. T. Dennis, G. C. Lalor, "Dietary intake of minerals and trace elements in rice on the Jamaican market", *J. Food Compos. Anal.* vol. 26, pp. 111-21, 2012.
- [18] S. Kelly, M. Baxter, S. Chapman, C. Rhodes, J. Dennis, P. Brereton, "The application of isotopic and elemental analysis to determine the geographical origin of premium long grain rice.", *Eur. Food Res. Technol.* vol. 214, pp. 72-78, 2002.
- [19] FAO-Food and Agriculture Organization of the United Nations. Report of the Eight Session of the Codex Committee on Contaminants in Foods, 2014.
- [20] EFSA, Dietary exposure to inorganic arsenic in the European population. EFSA Journal 2014, vol. 12(3):3597, 68 pp. doi:10.2903/j.efsa.2014.3597
- [21] Codex, Codex General Standard for Contaminants and Toxins in Food and Feed. Codex Alimentarius Commission, Rome, Italy, 1995 (Codex Standard 193-1995).
- [22] JECFA, 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, 2011, pp. 89.