WALAILAK JOURNAL
http://wjst.wu.ac.th Area-based Research

Analysis of Lead and Cadmium Contents in Local Vegetables in Surat Thani, Thailand

Nipaporn MEEPUN, Nattapan SAGUANSAKBARAMEE and Rattana WONGCHUPHAN*

Program of Chemistry, Faculty of Science and Technology, Suratthani Rajabhat University, Surat Thani 84100, Thailand

(***Corresponding author's e-mail: wongchuphanr@yahoo.com**)

Received: 5 January 2013, Revised: 12 March 2013, Accepted: 9 October 2013

Abstract

Two toxic heavy metals, cadmium (Cd(II)) and lead (Pb(II)), in samples of local vegetables were analyzed by graphite furnace atomic absorption spectroscopy (GFAAS). Pak-Leang (*Gnetum gnemon* Linn.), Pak-Waen (*Marsilea crenata* Presl.), Mun-Poo (*Glochidion littorale* Blume Baill.), and Chamuang (*Garcinia cowa* Roxb.) were from fresh markets in 4 districts namely Muang, Phunphin, Kanchanadit and Ban Na Doem, Surat Thani province. The preparation of samples was carried out by mixed acid digestion procedure in order to extract the heavy metals. From the GFAAS analysis of sample solutions, the average lead contents were as follows: 0.10 ± 0.11 mg kg^{-1} in Pak-Leang, 0.04 ± 0.07 mg kg^{-1} in Pak-Waen, 0.14 ± 0.17 mg kg^{-1} in Mun-Poo and 0.02 ± 0.05 mg kg^{-1} in Chamuang. The results indicated that the concentrations of lead within these local vegetables were under the maximum allowable level according to the standard of the Ministry of Public Health, Thailand. On the other hand, analysis of cadmium found that 3 certain vegetables including Pak-Waen (0.48 ± 0.27 mg kg^{-1}), Mun-Poo (0.78 ± 0.72 mg kg^{-1}) and Chamuang (0.34 ± 0.27 mg kg^{-1}), were contaminated with cadmium higher than the maximum allowable levels in the average for the standards of Australia-New Zealand, Codex, China and the European Union. The assessment of heavy metal indicated that these accumulation quantities in edible plants could be valuably evident for public concerns and research-based food safety.

Keywords: Lead, cadmium, local vegetables, atomic absorption spectrometry, Surat Thani

Introduction

Heavy metals are considered as trace elements because of their necessity and very restricted quantity in humans and for the survival of living things [1]. The traces of heavy metals in plants and animals arise through the absorption processes of naturally occurring soil components, and the consequences of human activity. These species cannot be degraded or destroyed easily by nature.

Vital nutrients, plants and animals are accompanied by taking up small amounts of heavy metal contaminants concentrating them. Definite heavy metals such as lead, cadmium, and mercury have been recognized to be potential toxic species within specific contamination limits, a substantial potential hazard occurs for human nutrition. Impact of increasing industrialization has been accompanied all over the world by the taking out and spreading of mineral constituents from their natural deposits. Through subsequent concentration, many of these have encountered chemical changes through technical processes and finally could be emitted, finely isolated and dissolved in aqueous solutions, by way of effluent [2-4], sewage [5,6], dumping site [7], into the water [8], the earth [9] and the outside air [10] and consequently into the food chain [11,12].

Surat Thani Province located on the eastern shore of the Gulf of Thailand has served as a mining industry for many decades. Likewise, neighboring provinces including Chumphon, Nakhon Si Thammarat, Krabi, Phang Nga and Ranong are responsible for natural mineral resources. Much of Thailand has encountered health hazard problems because of heavy metal pollution in the environment caused by old mining sites in Kanchanaburi, Nakhon Si Thammarat, and Pattani [13].

Atomic absorption spectroscopy is commonly used to determine chemical elements such as heavy metals based on the absorption of light by free atoms in the gaseous state [14]. Several techniques have been developed to vaporize the sample i.e. flame [15], and graphite-coated furnace [16,17]. Recently, emission spectroscopy such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [18] and anodic stripping voltammetry [19] has been proposed as a more advanced technology for the quantitative determination of heavy metals being less time-consuming and offering better sensitivity. The spectrophotometric procedure could be usefully applied in an environmental study by the way of undesirable toxic lead and cadmium which could distribute and contaminate foodstuffs and their surroundings. It is always difficult to assign a certain cause for an elevated heavy metal quantity. Indeed, even foodstuffs produced in entirely unpolluted areas are not completely free of heavy metals. The absorption of very small quantities is therefore inevitable theoretically and has always arisen. As a result, standards for heavy metal contamination levels in foodstuffs should be specified.

The aim of this study is to determine the levels of lead and cadmium in local vegetables available in four districts in Surat Thani province, Thailand. The local vegetables (**Figure 1**) including Pak-Leang (*Gnetum gnemon* Linn.), Pak-Waen (*Marsilea crenata* Presl.), Mun-Poo (*Glochidion littorale* Blume Baill.) and Chamuang (*Garcinia cowa* Roxb.) were selected due to their common intake. Also, the potential human hazard due to the consumption of various selected vegetables was evaluated by means of national and international criteria.

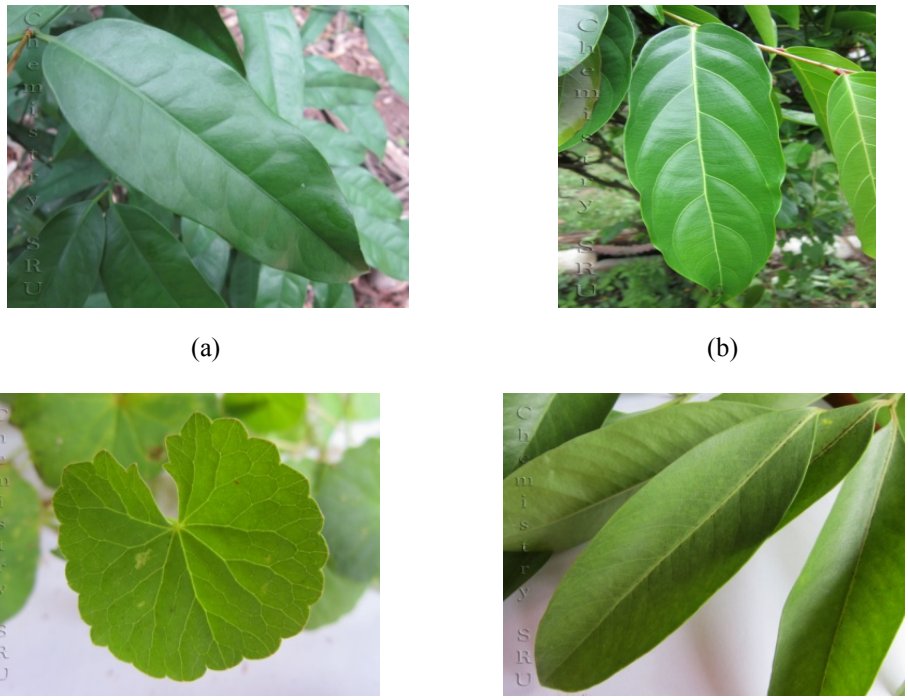

Figure 1 Four local vegetables available in Surat Thani province (a) Pak-Leang (b) Mun-Poo (c) Pak-Waen (d) Chamuang.

Materials and methods

Apparatus

All measurements were carried out with a Perkin-Elmer AAnalyst^{TM} 800 atomic absorption spectrophotometer. The concentrations of Pb(II) and Cd(II) were analyzed by graphite furnace AAS with high-frequency modulation polarization Zeeman correction of background absorption. Hollow cathode lamps were used as radiation sources for Pb and Cd. Analytical absorbance signals were measured at wavelengths 283.3 nm for Pb and 228.8 nm for Cd.

Reagents

All reagents used were analytical reagent grade. The concentrated nitric acid (conc. HNO_3), concentrated sulfuric acid (conc. H_2SO_4) and concentrated perchloric acid (conc. $HClO_4$) were supplied by Merck (Germany). All standard solutions were prepared by diluting 1000 ppm of a Pb(II) and Cd(II) standard solution (Merck, Germany) with deionized water.

Sample collection

The study was performed by random selection from different areas in Surat Thani province specifically Muang, Phunphin, Kanchanadit and Ban Na Doem districts. The selected vegetable samples were available in particular places of each area where applicable and according to their seasonal availability.

At the time of sample collection (December 2011 to February 2012), the local vegetables including Pak-Leang, Pak-Waen (Water Clover in English), Mun-Poo and Chamuang (Cowa in English) were collected from fresh markets in the selected areas. A total of 18 fresh leaf samples included **Pak-Leang** from 6 sampling sites (Sampaothong, Don Nok, Suratthani Hospital markets in Muang district; Co-op market in Phunphin district; Thathong Mai market, Kanchanadit district; Railway Station market, Ban Na Doem district), **Pak-Waen** from 5 sampling sites (Sampaothong, Suratthani Hospital, and Don Nok markets, Muang district; Kamnan Duan, Ban Na Doem district; Thathong Mai, Kanchanadit district), **Mun-Poo** from 3 sampling sites (Kamnan Duan and Railway Station markets, Ban Na Doem district; Suratthani Hospital market, Muang district), and **Chamuang** from 4 sampling sites (Sampaothong and Don Nok markets, Muang district; Co-op market, Phinphin district; Kamnan Duan market, Ban Na Doem district).

Sample preparation

Sample solutions were prepared using a mixed acid procedure (conc. HNO_3, conc. H_2SO_4 and conc. $HClO_4$ = 5:1:1 by volume) of dried and finely ground vegetable samples. The samples were digested to extract the heavy metals by heating at 40 °C until a clear solution was observed. The filtered solutions were added to deionized water to 50 mL for GFAAS analysis. The furnace program [temperature (^{o}C)/ramp time (s)/hold (s)] employed for Pb(II) determination was drying (110 °C/10 s/30 s; 130 °C/5 s/44 s), pyrolysis (750 °C/10 s/30 s), atomization (1400 °C/0 s/5 s) and cleaning (2450 °C/1 s/4 s). A similar furnace program was performed for the determination of Cd(II) with the exception of the temperature for pyrolysis (500 °C) and atomization (1350 °C). 10 % (w/v) $H_2PO_4NH_4$ was used as the matrix modifier in the analysis process.

Results and discussion

Analytical performance

Under the optimum conditions, the linear concentration of the analytes ranged from 0 to 20.0 μg L^{-1} for Pb(II) and 0 to 5.0 μg L^{-1} for Cd(II). The recoveries in the real samples spiked with Pb(II) and Cd(II) were determined, and found to be 98.09 and 101.98 % for Pb(II) and Cd(II), respectively. The limit of detection (LOD) estimated as 3 times in the standard deviation for low Pb(II) and Cd(II) concentration, was found to be 0.05 mg kg^{-1} for Pb(II) and 0.06 mg kg^{-1} for Cd(II). The reproducibility of the method

was checked by successive measurements (n = 7) of 4.0 μg L^{-1} Pb(II) and 3.0 μg L^{-1} Cd(II), and the percent of relative standard deviation (% RSD) were 3.16 and 5.71 %, respectively.

Sample analysis

After sample preparation, the solution containing Pb(II) and Cd(II) was analyzed by GFAAS and the average concentrations found in each vegetable sample are shown in **Table 1**.

From the lead analysis, the average values indicate acceptable Pb(II) contamination levels in samples such as 0.10 ± 0.11 mg kg^{-1} for Pak-Leang, 0.14 ± 0.17 mg kg^{-1} for Mun-Poo, 0.04 ± 0.07 mg kg^{-1} for Pak-Waen, and 0.02 ± 0.05 mg kg^{-1} for Chamuang, according to the limit of the Ministry of Public Health, Thailand in food (1.0 mg kg^{-1}) [20]. International standards including the Codex and China maximum levels in food by 0.3 mg kg^{-1} were also applied [21-23], resulting in lower Pb contamination for all vegetables. The concentrations of lead accumulated in Pak-Leang and Mun-Poo leaves appear in a broad range. With more restriction of the standards of European Union and Australia-New Zealand (0.2 mg kg^{-1}) [24-26], there was strong evidence that greater Pb(II) levels in these 2 samples occurred by 0.24 ± 0.09 mg kg^{-1} (Railway Station market, Ban Na Doem district) for Pak-Leang, and 0.27 ± 0.22 mg kg^{-1} (Kamnan Duan market, Ban Na Doem district) for Mun-Poo. This may be due to past mining sites, leading to elevated lead contamination in soil and water resources [3,5].

Table 1 Cd and Pb contents in four different vegetable samples by graphite furnace atomic absorption spectrometry

Sample No.	Vegetables	Cd(II) (mg kg^{-1})	Pb(II) (mg kg^{-1})
		Mean ± SD	Mean ± SD
1	Pak-Leang	0.08 ± 0.04	0.10 ± 0.11
2	Mun-Poo	0.78 ± 0.72	0.14 ± 0.17
3	Pak-Waen	0.48 ± 0.27	0.04 ± 0.07
4	Chamuang	0.34 ± 0.27	0.02 ± 0.05
% Recovery		101.98	98.09
% RSD		5.71	3.16
[1]Thailand maximum allowable levels of contaminants in vegetables		not specified	1.0
[2]China maximum levels of contaminants in leafy vegetables		0.2	0.3
[3]Codex maximum levels for contaminants in food		0.2	0.3
[4]Food standard European Communities		0.2	0.2
[5]Food standard Australia-New Zealand		0.1	0.2

[1]Notified by the Thai Ministry of Public Health, 2553 (2010), Food Act B.E. 2522 (1979).
[2]Cited in Cao *et al*., 2010, p. 1795.
[3]Codex Alimentarius Commission, 2001 and 2004. (cited in Kachenko and Singh, 2006)
[4]Commission European Communities, 2001.
[5]ANSTAT, 2001. (cited in Kachenko and Singh, 2006).

The average concentrations of cadmium for all vegetable samples are shown in **Table 1**. The acceptable cadmium contamination in selected local vegetables was evaluated based on international criteria. The wide range of average cadmium concentration, for instance, 0.78 ± 0.72 mg kg^{-1} for Mun-Poo, 0.48 ± 0.27 mg kg^{-1} for Pak-Waen, and 0.34 ± 0.27 mg kg^{-1} for Chamuang, reflects a greater distinction in Cd(II) concentration in comparison of each vegetable collected from different sampling

sites. The following results provide further details on the cadmium concentrations in particular sampling sites (**Table 2**). Pak-Waen was contaminated with Cd(II) ranging from 0.18 to 0.86 mg kg^{-1} while Mun-Poo showed levels from 0.08 to 1.66 mg kg^{-1} and Chamuang from 0.17 to 0.78 mg kg^{-1}. Based on the maximum allowable levels of the Codex, China, and European Union [21-26], these vegetables did not meet these standards (0.2 mg kg^{-1}). In addition, the standard of Australia-New Zealand limits the maximum permissible level of 0.1 mg kg^{-1} [24]. On the other hand, Pak-Leang was only slightly contaminated with acceptable cadmium concentrations (0.08 ± 0.04 mg kg^{-1}). As a matter of fact, the identifying of heavy metal contamination in vegetables is still unclear due to a variety of potential contributors commonly including fertilizers, pesticides, fungicides, sewage, industrial effluent, and vehicular air pollutants [27].

Table 2 Cadmium concentrations in three vegetable samples by graphite furnace atomic absorption spectrometry. All measurements were in triplicates.

Samples	Cd(II) (mg kg^{-1})
	Mean ± SD
Pak-Waen	
S1	0.21 ± 0.06
S2	0.18 ± 0.01
S3	0.51 ± 0.02
S4	0.64 ± 0.03
S5	0.86 ± 0.13
Mun-Poo	
S6	0.57 ± 0.06
S7	1.66 ± 0.23
S8	0.08 ± 0.02
Chamuang	
S9	0.17 ± 0.01
S10	0.21 ± 0.03
S11	0.78 ± 0.08
S12	0.22 ± 0.08

Kamnan Duan (S1, S6, S12) and Railway Station (S7) markets, Ban Na Doem district
Sampaothong (S2, S10), Don Nok (S4, S11) and Suratthani Hospital (S5, S8) markets, Muang district
Thathong Mai (S3) market, Kanchanadit district
Co-op (S9) market, Phinphin district

Conclusions

The analysis of lead and cadmium contents revealed that the concentrations of lead and cadmium found in each type of local vegetables were different. Most local vegetables showed high concentrations of cadmium based on international criteria. Therefore, awareness of the potential health hazards of heavy metal contamination in food should be considered for long-term consumption. The outcome is useful for public food safety information. However, the seasonal change tends to be a major variable influencing heavy metal accumulation in edible plants. Consequently, the continuous evaluation of heavy metal contents should be taken to provide more information on the potential risks of toxic effects.

Acknowledgement

The research project was financially supported by Research and Development Institute of Suratthani Rajabhat University, Thailand.

References

[1] CG Fraga. Relevance, essentiality and toxicity of trace elements in human health. *Mol. Aspects Med.* 2005; **26**, 235-44.
[2] P Akkajit and C Tongcumpou. Fractionation of metals in cadmium contaminated soil: relation and effect on bioavailable cadmium. *Geoderma* 2010; **156**, 126-32.
[3] R Honda, W Swaddiwudhipong, M Nishijo, P Mahasakpan, W Teeyakasem, W Ruangyuttikarn, S Satarug, C Padungtod and H Nakagawa. Cadmium induced renal dysfunction among residents of rice farming area downstream from a zinc-mineralized belt in Thailand. *Toxicol. Lett.* 2010; **198**, 26-32.
[4] A Singh and M Agrawal. Effects of municipal waste water irrigation on availability of heavy metals and morphophysiological characteristics of *Beta vulgaris* L. *J. Environ. Biol.* 2010; **31**, 727-36.
[5] S Karnchanawong and P Limpiteeprakan. Evaluation of heavy metal leaching from spent household batteries disposed in municipal solid waste. *Waste Manag.* 2009; **29**, 550-8.
[6] S Prabpai, L Charerntanyarak, B Siri, MR Moore and BN Noller. Effects of residues from municipal solid waste landfill on corn yield and heavy metal content. *Waste Manag.* 2009; **29**, 2316-20.
[7] T Prechthai, P Parkpian and C Visvanathan. Assessment of heavy metal contamination and its mobilization from municipal solid waste open dumping site. *J. Hazard. Mater.* 2008; **156**, 86-94.
[8] O Krissanakriangkrai, W Supanpaiboon, S Juwa, S Chaiwong, W Swaddiwudhipong and KA Anderson. Bioavailable cadmium in water, sediment, and fish, in a highly contaminated area on the Thai-Myanmar border. *Thammasat Int. J. Sci. Tech.* 2009; **14**, 60-8.
[9] U Unhalekhaka and C Kositanont. Distribution of cadmium in soil around zinc mining area. *Thai J. Toxicol.* 2008; **23**, 170-4.
[10] S Sharma and FM Prasad. Accumulation of lead and cadmium in soil and vegetable crops along major highways in Agra (India). *Electron. J. Chem.* 2010; **7**, 1174-83.
[11] A Kumar, IK Sharma, A Sharma, S Varshney and PS Verma. Heavy metals contamination of vegetable foodstuffs in Jaipur (India). *Electron. J. Environ. Agri. Food Chem.* 2009; **8**, 96-101.
[12] R Apinan, S Satarug, R Ruengweerayut, W Tassaneeyakul and K Na-Bangchang. Cadmium exposure in Thai populations from central, northern and northeastern Thailand and the effects of food consumption on cadmium levels. *Southeast Asian J. Trop. Med. Public Health* 2009; **40**, 177-86.
[13] Pollution Control Department, Ministry of Natural Resources and Environment. Available at: http://wqm.pcd.go.th/water/images/stories/planing/reports/2555/wqmsummary2554.pdf, accessed July 2012.
[14] RK Sharma, M Agrawal and FM Marshall. Heavy metal (Cu, Zn, Cd and Pb) contamination of vegetables in urban India: a case study in Varanasi. *Environ. Pollut.* 2008; **154**, 254-63.
[15] R Subramanian, S Gayathri, C Rathnavel and V Raj. Analysis of mineral and heavy metals in some medicinal plants collected from local market. *Asian Pacific J. Trop. Biomed*. 2012; S7-S78.
[16] Z Ajtony, N Szoboszlai, EK Suskó, P Mezei, K György and L Bencs. Direct sample introduction of wines in graphite furnace atomic absorption spectrometry for the simultaneous determination of arsenic, cadmium, copper and lead content. *Talanta* 2008; **76**, 627-34.
[17] N Al-Chaarani, JH El-Nakat, PJ Obeid and S Aouad. Measurement of levels of heavy metal contamination in vegetables grown and sold in selected areas in Lebanon. *Jordan J. Chem.* 2009; **4**, 303-15.
[18] AG Kachenko and B Singh. Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. *Water Air Soil Pollut.* 2006; **169**, 101-23.

[19] U Injang, P Noyrod, W Siangproh, W Dungchai, S Motomizu and O Chailapakul. Determination of trace heavy metals in herbs by sequential injection analysis-anodic stripping voltammetry using screen-printed carbon nanotubes electrodes. *Anal. Chim. Acta* 2010; **668**, 54-60.
[20] Thai Ministry of Public Health, Standard of Contaminated Food, Available at: http://www.dmsc.moph.go.th, accessed August 2012.
[21] Codex Alimentarius Commission. *Lead: Maximum Levels*. Vol I. Codex Stan 230, 2001.
[22] Codex Alimentarius Commission. *Report of the 34th Session of the Codex Committee on Food Additives and Contaminants*. Rotterdam, Netherlands, 2004.
[23] AG Kachenko and B Singh. Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. *Water Air Soil Pollut.* 2006; **169**, 101-23.
[24] Center of Excellent on Environment Health, Available at: http://www.etm.sc.mahidol.ac.th/a9.s-html, accessed September 2011.
[25] ANSTAT. *Australia and New Zealand Food Standards Code*. Vol II. ANSTAT, Victoria, 2001.
[26] Commission European Communities. Commission of the European Communities-Commission regulation (EC) No 466/2001 of 8 March 2001 setting maximum levels for certain contaminants in foodstuffs. *Official J. Eur. Comm.* 2001; **L77**, 1-13.
[27] F Marshall, R Agarwal, D Lintelo, DS te Bhupal, RPB Singh, N Mukherjee, C Sen, N Poole, M Agrawal and SD Singh. Heavy metal contamination of vegetables in Delhi. Available at: http://toxicslink.org/docs/06102_Finding_of_Heavy_Metal_Contamina-tion_of_Vegetables.pdf, accessed June 2012.