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)

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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™ 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. HNO₃), concentrated sulfuric acid (conc. H₂SO₄) and concentrated perchloric acid (conc. HClO₄) 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, Phunpin, 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 (Sampaonthong, Don Nok, Suratthani Hospital markets in Muang district; Co-op market in Phunphin district; Thatthong Mai market, Kanchanadit district; Railway Station market, Ban Na Doem district), Pak-Waen from 5 sampling sites (Sampaonthong, Suratthani Hospital, and Don Nok markets, Muang district; Kamnan Duan, Ban Na Doem district; Thatthong 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 (Sampaonthong and Don Nok markets, Muang district; Co-op market, Phunphin district; Kamnan Duan market, Ban Na Doem district).

Sample preparation
Sample solutions were prepared using a mixed acid procedure (conc. HNO₃, conc. H₂SO₄ and conc. HClO₄ = 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 (°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) H₃PO₄-NH₄ 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
Analysis of Some Heavy Metals in Local Vegetables
Nipaporn MEEPUN et al.

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was checked by successive measurements \((n = 7)\) of 4.0 \(\mu g\) L\(^{-1}\) Pb(II) and 3.0 \(\mu g\) 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

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Vegetables</th>
<th>Cd(II) (mg kg(^{-1}))</th>
<th>Pb(II) (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
</tr>
<tr>
<td>1</td>
<td>Pak-Leang</td>
<td>0.08 ± 0.04</td>
<td>0.10 ± 0.11</td>
</tr>
<tr>
<td>2</td>
<td>Mun-Poo</td>
<td>0.78 ± 0.72</td>
<td>0.14 ± 0.17</td>
</tr>
<tr>
<td>3</td>
<td>Pak-Waen</td>
<td>0.48 ± 0.27</td>
<td>0.04 ± 0.07</td>
</tr>
<tr>
<td>4</td>
<td>Chamuang</td>
<td>0.34 ± 0.27</td>
<td>0.02 ± 0.05</td>
</tr>
<tr>
<td>% Recovery</td>
<td></td>
<td>101.98</td>
<td>98.09</td>
</tr>
<tr>
<td>% RSD</td>
<td></td>
<td>5.71</td>
<td>3.16</td>
</tr>
</tbody>
</table>

1Thailand maximum allowable levels of contaminants in vegetables
2China maximum levels of contaminants in leafy vegetables
3Codex maximum levels for contaminants in food
4Food standard European Communities
5Food standard Australia-New Zealand

2Cited in Cao et al., 2010, p. 1795.

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.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cd(II) (mg kg⁻¹)</th>
<th>Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pak-Waen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>0.21 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>0.18 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>0.51 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>0.64 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>0.86 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>Mun-Poo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>0.57 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>1.66 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>S8</td>
<td>0.08 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Chamuang</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S9</td>
<td>0.17 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>S10</td>
<td>0.21 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>S11</td>
<td>0.78 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>S12</td>
<td>0.22 ± 0.08</td>
<td></td>
</tr>
</tbody>
</table>

Kamnan Duan (S1, S6, S12) and Railway Station (S7) markets, Ban Na Doem district
Sampaotong (S2, S10), Don Nok (S4, S11) and Surathani 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

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References

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