CONCENTRATIONS OF CADMIUM AND ARSENIC IN SEAFOOD FROM MUANG DISTRICT, RAYONG PROVINCE

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ABSTRACT: This study was designed to determine the concentration of cadmium (Cd) and arsenic (As) in seafoods from Muang District, Rayong Province. Between January and February 2008, samples of the 13 most consumed seafood species were selected and randomly obtained from 3 local markets in Muang District of Rayong Province. Cadmium and arsenic levels were measured by atomic absorption spectrophotometry (AAS). The concentration of cadmium in these seafoods were 0.009 – 0.731 μg/g with the highest of 0.731 μg/g in blood cockle (Arca granulosa). The concentration of arsenic in these seafoods were 0.401 – 7.032 μg/g with the highest of 7.032 μg/g in soft cuttle fish (Sepioteuthis lessoniana). This study revealed that the concentrations of two heavy metals accumulated in 13 kinds of seafoods from Muang District, Rayong Province were within safety levels for consumers since cadmium concentration was lower than the allowable standard level of food issued by the National Health and Medical Research Council, Australia and the European Union, and that of arsenic content was not higher than the allowable standard level of food issued by the Ministry of Public Health of Thailand, with the exception of the total arsenic contents in soft cuttle fish (Sepioteuthis lessoniana), splendid squid (Loligo duvauceli), yellow stripe trevally (Selaroides leptolepis), ornate threadfin bream (Nemipterus hexodon) and green mussel (Perna viridis).

Key words: Cadmium, Arsenic, seafood, atomic absorption spectrophotometry, Rayong

INTRODUCTION: Environmental pollution represents a major problem in both developed and underdeveloped countries. Thailand is one of the countries which suffers from high biosphere pollution (air, soil and water), especially the east of Thailand, because it is an industrialized area.

Heavy metals have long been recognized as one of the most important pollutants in the coastal waters of Rayong Province because of their toxicity and capacity to accumulate in marine organisms. The main source of heavy metal pollution comes from discharge of untreated effluents from metal-related industries, such as electroplating, manufacturing of batteries, and petrochemical industries. Cadmium and arsenic are also potential environmental hazard. Cadmium has an extremely long residence time (over 20 years) in the human body and a significant proportion of the body burden is stored in the liver and kidney. Ingestion of large doses (>300 mg) of cadmium may be fatal. Long exposure to high doses of cadmium may cause biochemical and functional changes in some critical organs.

Arsenic and many of its compounds are toxic metals. Living organisms are exposed to this metal primarily from food and water. Ingestion of large doses (70-180 mg) of arsenic may be fatal. Exposure to arsenic can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects. The objective of this study was to determine the concentrations of cadmium and arsenic in seafood from Muang District, Rayong Province. And then to compare the results obtained with the standard level of food issued by the National Health and Medical Research Council, Australia and the European Union for cadmium and the Ministry of Public Health of Thailand for arsenic.

MATERIALS AND METHODS:
Sample

During the period from October to December 2007, the food frequency questionnaire of seafoods was carried out with primary health care voluntary staff of Muang District, Rayong Province (n = 316). The questionnaire showed 13 kinds of seafood which were the mostly consumed by the subjects (table 1). These 13 kinds of seafoods were selected and randomly obtained from 3 local markets in Muang District of Rayong Province.
markets in Muang District. A total of 39 samples (3 samples for each kind of seafoods from 3 local markets) were analyzed for cadmium and arsenic concentrations by atomic absorption spectrophotometry (AAS).4)

**Instruments**

Determination of cadmium was performed with graphite furnace atomic absorption spectrophotometry (GFAAS) (AAnalyst 600, Perkin Elmer). Determination of total arsenic was performed with a flow injection hydride generation atomic absorption spectrophotometry (FI-HG-AAS) (AAS 3300/ FIAS 100, Perkin Elmer). Other equipment used included a microwave digestion unit (mls1200 mega, Milestone), a muffle furnace (ECF 12/30,Lenton) and blender. All glassware was treated with 20% (v/v) nitric acid (HNO3) for 24 hours, and then rinsed three times with deionized water before use.

**Reagents**

All reagents used were of analytical grade except supra pur 65% nitric acid. Deionized water (18MΩ.cm) was used for the preparation of reagents and standards. Commercial standard solutions (1000 mg/l) of cadmium and arsenic were used (Perkin Elmer). The working standard solutions were freshly prepared by diluting an appropriate aliquot of the standard stock solutions.

**Sample preparation**

The entire edible part of each sample was homogenized in a blender and kept at 4 °C until the analysis.

**Cadmium determination**

The sample (2 g) was placed into digestion vessel and 5 ml of 65% HNO3 was added. The vessel was closed with a set of lid and placed inside the microwave oven. Samples were irradiated at 250 W for 1 minute, 0 W for 2 minutes, 250 W for 5 minutes, 400 W for 5 minutes and 600 W for 5 minutes. After digestion, the vessels were cooled to room temperature and diluted with deionized water to final volume of 25 ml (sample solution).

The quantification of cadmium was performed with GFAAS. The furnace program [temperature (°C)/ ramp time [s] / hold time [s]] employed for cadmium determination was: drying (110 °C/ 1 s/ 30 s; 130 °C/ 5 s/ 35 s); pyrolysis (550 °C/ 10 s/ 20 s); atomization (1350 °C/ 0 s/ 3 s); cleaning (2450 °C/ 1 s/ 3 s). The matrix modifier used for determining this metal was a mixture of H3PO4NH4 0.05 mg and Mg(NO3)2 0.003 mg in deionized water. The quantification was performed by using a calibration curve of the corresponding standards.

**Arsenic determination**

Ten milliliters of each sample solution (from cadmium determination) was placed into crucible dish and treated with 1 ml of 7.5% (w/v) Mg(NO3)2 solution. The mixtures were heated on hot plate at low heat to dryness and increased heat to 375°C. Dried samples were oxidized for any carbonaceous matter and decompose excess Mg(NO3)2 in 450 °C furnace about 30 minutes. The ash was dissolved in 2 ml 8M HCl and reduced with 2 ml concenrate HCl and 2 ml of reducing solution [5% (w/v) ascorbic acid + 5% (w/v) KI], let stand 45 minutes. After that, it was diluted with deionized water into 20 ml volumetric flask.

The analytical conditions for arsenic determination by FI-HG-AAS were the following : loop sample, 500 µL; reducing agent, 0.2% (w/v) NaBH4 in 0.05% (v/v) NaOH, 5 mL/min flow rate; HCl 10% (v/v), 10 mL/min flow rate; carrier gas argon, 50 mL/min flow rate; wavelength, 193.7 nm; slit 0.7 nm; lamp current setting 400 mA; cell temperature 900 °C. Calibration standard solution of As(III) were prepared from a stock standard solution of arsenic oxide (As2O3), added concenrate hydrochloric acid and reducing solution mixture containing 5% (w/v) KI and 5% (w/v) ascorbic acid same as sample solution.

**Quality Control**

Duplicate analyses were performed for each sample. The limit of quantitation (LOQ) for cadmium and arsenic was 0.009 µg/g and 0.053 µg/g respectively. A recovery test was carried out by spiking of standard solutions of heavy metals in homogenized samples. The recovery for cadmium and arsenic, which analyzed under the experimental conditions were found to be between
80 – 110 %. Duplicate analysis were performed in each set of the sample and the relative percent difference (% RPD) were within the acceptable limit.

RESULTS:

Seafood consumption

There were 316 participants in our study. They included 26 males and 290 females aged between 30 to 65 years old. The results of the dietary survey identified the 13 species of seafoods that were most frequently consumed by the subjects. These seafoods were classified into 4 groups: fish, bivalves, cephalopods and crustaceans (table 1). About 89% of subjects reported consuming yellow-tail round scad (*Decapterus maruadsi*) and indian mackerel (*Rastrelliger kanagurta*) at least 4-5 times/week. 85% of subjects ate ornate threadfin bream (*Nemipterus hexodon*) and yellow stripe trevally (*Selaroides leptolepis*) at least 2-3 times/week. Among other kinds of seafoods were

<table>
<thead>
<tr>
<th>Scientific name</th>
<th>Common name</th>
</tr>
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<tbody>
<tr>
<td><em>Decapterus maruadsi</em></td>
<td>Yellow-tail round scad (ปลาทูแขก)</td>
</tr>
<tr>
<td><em>Rastrelliger kanagurta</em></td>
<td>Indian mackerel (ปลาลัง)</td>
</tr>
<tr>
<td><em>Nemipterus hexodon</em></td>
<td>Ornate threadfin bream (ปลาทรายแดง)</td>
</tr>
<tr>
<td><em>Selaroides leptolepis</em></td>
<td>Yellow stripe trevally (ปลาขางเหลือง)</td>
</tr>
<tr>
<td><em>Scomberomorus commerson</em></td>
<td>Spanish mackerel (ปลาอินทรีย์)</td>
</tr>
<tr>
<td><em>Thunnus tonggol</em></td>
<td>Longtail tuna (ปลาโอ)</td>
</tr>
<tr>
<td><em>Parastromateus niger</em></td>
<td>Black pomfret (กุ้งแชบือ)</td>
</tr>
<tr>
<td><em>Epinephelus tauvina</em></td>
<td>Greasy grouper (ปลาเก่า)</td>
</tr>
<tr>
<td><em>Perna viridis</em></td>
<td>Green mussel (หอยแมลงภู่)</td>
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<tr>
<td><em>Arca granulose</em></td>
<td>Blood cockle (หอยแครง)</td>
</tr>
<tr>
<td><em>Sepioteuthis lessoniana</em></td>
<td>Soft cuttlefish (หมึกหอม)</td>
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<tr>
<td><em>Loligo duvauceli</em></td>
<td>Splendid squid (หมึกกล้วย)</td>
</tr>
<tr>
<td><em>Penaeus merguiensis</em></td>
<td>Banana shrimp (กุ้งแชบือ)</td>
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Table 1 13 Types of seafood which were the most commonly consumed by the subjects of Muang District, Rayong Province

![Figure 1](image-url)  
**Figure 1** Mean concentration of cadmium and arsenic in 13 kinds of seafoods
consumed very frequently.

**Heavy metal concentration**

Figures 1 show mean concentrations of cadmium and arsenic in each kind of seafood. Content less than the limit of quantitation was taken as being equal to the limit of quantitation for the purpose of calculating intake. The concentration of cadmium in these seafood was 0.009 – 0.731 µg/g with the highest of 0.731 µg/g in the bivalve group (blood cockle). The concentration of arsenic in these seafood was 0.401 – 7.032 µg/g with the highest of 7.032 µg/g in the cephalopod group (soft cuttle fish).

However, the contamination level of cadmium in these kinds of seafoods was still lower than the standard limited level of food issued by the National Health and Medical Research Council, Australia and the European Union, and that of arsenic concentration was not higher than the standard limited level of food issued by the Ministry of Public Health of Thailand, with the exception of the total arsenic level in yellow stripe trevally, ornate threadfin bream, green mussel, soft cuttle fish and splendid squid.

**DISCUSSION:**

Cadmium is known to accumulate in the human kidney for a relatively long time, from 20 to 30 years, and, at high doses, is also known to produce health effects on the respiratory system, induce the renal and hepatic toxicity and has been associated with bone disease. In Japan, Itai-Itai disease was found to be caused by high intakes of cadmium contaminated in rice. In this study, the cadmium content in bivalves (0.731 µg/g in blood cockle and 0.140 µg/g in green mussel) was higher than for other groups. The highest cadmium level was found in the blood cockle. Bruhn et al., (1999) found high level of this metal in bivalves from various areas of Chilean coast. Furthermore, Vibunpant et al., (2006) found that the level of this metal in bivalves and crustacean from the southern coast of the Gulf of Thailand was higher than other groups. The shellfish group has high concentration of cadmium because cadmium can accumulate in shellfish in the form of cadmium-binding peptides.

Mean concentrations of cadmium in seafoods found in Catalonia, Spain (0.037 µg/g) and those found in United Kingdom (0.013 µg/g) were lower than those obtained from this study (0.082 µg/g). Moreover, Vibunpant et al., (2008) found that the concentration of cadmium in seafoods in the Andaman sea was lower than those obtained from this study. Since Rayong is an industrial area, environmental pollutants are released through waste products and contaminants into surface runoff into the water due to rain. The principal sources of pollution include chemical plants, oil refineries, petrochemical plants, PVC factories, metals production factories and plastics factories. In this way, the toxic chemicals are concentrated upward within food chains.

However, the mean concentration of cadmium in 13 kinds of seafoods reported in this study did not exceed the contamination standard limited level of the National Health and Medical Research Council, Australia (2 µg/g). Maximum cadmium content set by the European Union (EU) in fish, crustaceans, and bivalves/cephalopods are 0.1, 0.5 and 1 µg/g respectively. In this study, none of seafood samples had cadmium contents that exceeded the limits of EU legislation. There is no standard limited level for this metal in Thailand.

The cadmium content of food is just one of a number of factors which determines the actual uptake of cadmium into the body, overall nutritional status is a more important determinant of cadmium uptake into the body than is the actual amount of cadmium ingested. For example, iron deficiency is a more important determinant of cadmium uptake than is the actual amount of cadmium ingested.

Both organic and inorganic arsenic are present in varying amount in food. Marine organisms contain relatively high concentrations of organic arsenic. However, inorganic forms of arsenic are much more toxic than the organic forms. Inorganic arsenic is cause of human cancer at several sites and causes a variety of adverse health effects to humans after acute and chronic exposures. In Japan, in the mid-1950s, more than 100 infants died from arsenic poisoning.
Arsenic was identified from the dried milk that the infants had ingested. In Taiwan, there is also evidence that arsenic causes human kidney and bladder cancer. In the present study, we found that the total arsenic content in cephalopods (5.807 µg/g in splendid squid; 7.032 µg/g in soft cuttle fish) was higher than that in fish, bivalves and crustaceans. This result was similar to the result of Delgado et al. (2003). They found that the cephalopod group had higher arsenic content than the fish group, and bivalve group. Mean arsenic content in seafoods in this study (2.329 µg/g) was lower than that found in studies conducted in other locations: Basque country (Spain) 3.633 µg/g; United Kingdom 4.4 µg/g. However, the arsenic level in seafoods in Canada (1.662 µg/g); Catalonia, Spain (2.21 µg/g) and Santiago, Chile (1.351 µg/g) was lower than the arsenic level in this study.

The Ministry of Public Health of Thailand permits 2 µg/g for total arsenic and if it is higher than that, it must be analyzed for inorganic arsenic content. The maximum inorganic arsenic limit is 2 µg/g. In this study, the total arsenic content of yellow strip trevally, ornate threadfin bream, green mussel, soft cuttle fish, and splendid squid were above the maximum limits permitted in the Ministry of Public Health of Thailand. In this study, we could not analyze inorganic arsenic content. However, it is well known that most arsenic found in marine organisms is of an organic form, which is the less toxic form of this element because it is rapidly excreted in the urine.

CONCLUSION: The contamination levels of heavy metals in 39 samples of 13 kinds of seafoods in this study were still lower than contamination standard limited levels, with the exception of the total arsenic content in soft cuttlefish, splendid squid, yellow stripe trevally, ornate threadfin bream and green mussel, which were higher than the limit. These seafood types should be analyzed for inorganic arsenic level because inorganic forms of arsenic are much more toxic than the organic forms.

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REFERENCES:
and Development Bureau, Department of Fisheries, Ministry of Agriculture and Cooperatives.11: 1-37.


27. Notification of Ministry of Public Health No.98/2529 (1986) Standard for foods with contamination, which are sufficiently supported.
