Determination of Heavy Metal Residues in Tropical Fruits near Industrial Estates in Rayong Province, Thailand: A Risk Assessment Study

Amara Apilux[1], Thitiporn Thongkam[1], Thitaporn Tusai[2], Phasit Petisiwaveth[3], and Sumana Kladsomboon[3*]

[1]*Department of Clinical Chemistry, Faculty of Medical Technology, Mahidol University, Nakhon Pathom 73170, Thailand*
[2]*Community Health Care Service, Faculty of Medical Technology, Mahidol University, Bangkok 10700, Thailand*
[3]*Department of Radiological Technology, Faculty of Medical Technology, Mahidol University, Nakhon Pathom 73170, Thailand*

ARTICLE INFO

Received: 3 Jul 2022
Received in revised: 20 Sep 2022
Accepted: 26 Sep 2022
Published online: 31 Oct 2022
DOI: 10.32526/ennrj/21/202200146

Keywords:
Heavy metals/ Tropical fruits/ Health risk assessment/ Atomic Absorption Spectrometry/ Inductively Coupled Plasma-Mass Spectrometry/ Rayong Province

*** Corresponding author:**
E-mail: sumana.kla@mahidol.edu

ABSTRACT

This study determined the extent of heavy metal contamination of local fruit in Rayong, Thailand, an area where an industrial base is adjacent to agricultural areas. Dietary exposure to agricultural products grown in contaminated areas can cause multiple adverse effects to the human body. In order to avoid such undesirable effects, concentrations of heavy metals [arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn)] were investigated in popular tropical fruits from three districts of Rayong, namely Wang Chan, Klang and Mueang. The levels of heavy metals were determined by inductively coupled plasma- mass spectrometry (ICP-MS) and cold vapor-atomic absorption spectrometry (CV-AAS). Levels of the six heavy metals in sampled fruits (durian, jackfruit, pineapple, rambutan, long kong, and mangosteen) were in the range of 0.0004-6.7095 mg/kg; 16.7% of fruit samples exceeded maximum permissible limits of Pb. Based on health risk assessments, values of estimated daily intake (EDI) were less than those of maximum tolerable daily intake. However, for non-carcinogenic risks, high hazard index (HI) values were found in some markets while for carcinogenic risks (CRs), CR values of three fruits (durian, jackfruit, and mangosteen) exceeded acceptable levels. Therefore, long-term fruit consumption could impact health of local consumers. These results provided insight into the need for regular monitoring of heavy metal concentrations in potentially contaminated fruits and for prevention of its potential effects.

1. INTRODUCTION

Fruits are rich sources of important nutrients including folate, magnesium, potassium, calcium, and vitamins A and C (Striegel et al., 2018; Wanwimolruk et al., 2015; Swami et al., 2012; Ketsa et al., 2020). Thus, fruit consumption helps to maintain nutritional health and prevent illness (including cancers, and cardiovascular, neurological and gastrointestinal diseases) (Hurst and Hurst, 2012). Due to these benefits, fruits are increasingly recommended for daily consumption by the World Health Organization (FAO/WHO, 2003). But these health benefits may be overwhelmed when the fruits are contaminated.

Heavy metals are widely used in several aspects of agriculture and in a number of industries, and so may be parts of emissions into the environment (soil, water, or air) (Kinuthia et al., 2020; Lorestani et al., 2020; Ojekunle et al., 2022). In general, plants absorb metals essential for growth from cultivated soil, water, and even air. However, plants can also absorb toxic metals from contaminated environments (Lactusu et al., 1996; Big et al., 2012). These metals may not be biodegradable and have long biological half-lives, making them prone to accumulation in fruits and human consumers, potentially leading to adverse health effects (Kim et al., 2015; Dorsey et al., 2004). For example, vomiting, abdominal pain, dehydration,

Citation: Apilux A, Thongkam T, Tusai T, Petisiwaveth P, Kladsomboon S. Determination of heavy metal residues in tropical fruits near Industrial Estates in Rayong Province, Thailand: A risk assessment study. Environ. Nat. Resour. J. 2023;21(1): 19-34. (https://doi.org/10.32526/ennrj/21/202200146)

lung irritation, liver damage, and neurological problems were found to occur with long-term heavy metal consumption (Järup, 2003; Kim et al., 2015; FAO/WHO, 2011). Thus, heavy metal contamination of fruit is an important concern in the maintenance of human health and greater monitoring of heavy metal contamination is needed.

Thailand is a developing country in which expansion of industrial facilities is often in close proximity to agriculture. The number of industrial estates and parks has increased in each province, especially in the central and eastern parts of the country (such as Ayutthaya, Pathumthani, Samut Sakhon, Bangkok, Samut Prakan, Chonburi, Saraburi, and Rayong). Along with this industrialization, contamination of the environment and of agricultural products has been reported repeatedly [For example, in Ayutthaya (Kladsomboon et al., 2020; Klinsawathom et al., 2017), Loei (Pamonpol and Tokhun, 2019), Nakhon Pathom (Choprathumma et al., 2019), Pathumthani (Jankeaw et al., 2015), and Rayong (Kerdthep et al., 2009; Simasuwannarong et al., 2012; Nilkarnjanakul et al., 2022)].

Rayong Province lies in eastern Thailand, adjacent to major economic provinces (Chonburi and Chachoengsao). The Eastern Economic Corridor project (Dunseith, 2018) has transformed Rayong into Thailand's hub for manufacturing, research, and service support to export-oriented industries. However, 65.8% of its total area is still agricultural and many popular tropical fruits (such as durian, mangosteen, jackfruit, mango, pineapple, rambutan, and long kong) are grown mainly in this area (Rayong Provincial Government Center, 2020). As a result of these changes, fruits are often grown near the industrial development zone and are at risk of contamination. Despite these risks, heavy metal contamination in Rayong fruits has not been investigated.

Therefore, this study was designed to investigate possible heavy metal (Cu, Zn, As, Cd, Pb, and Hg) contamination of popular tropical fruits (durian, mangosteen, jackfruit, pineapple, rambutan, and long kong) of Rayong Province. Residue levels of heavy metals found in fruits were compared with permissible limits set by the Ministry of Public Health of Thailand (MoPH), the Food and Agriculture Organization (FAO) of the United Nations, the World Health Organization (WHO) and the European Union (EU). Furthermore, health risk assessment which is an essential tool for evaluating the possible health effects caused by contaminants was evaluated using estimated daily intake (EDI), target hazard quotient (THQ), hazard index (HI), and cancer risk (CR) (Xiao et al., 2017; Radfard et al., 2018). This work describes the methods and results of the study, providing useful information for health management and policy-making for prevention of heavy metal contamination and improved public health.

2. METHODOLOGY

2.1 Sampling

Six Thai fruits were targeted for study: durian (*Durio zibethinus* L.), jackfruit (*Artocarpus heterophyllus* Lam.), mangosteen (*Garcinia mangostana* L.), pineapple (*Ananas comosus* (L.) Merr.), rambutan (*Nephelium lappaceum* L.), and long kong (*Lansium parasiticum* (Osbeck) K.C.Sahni and Bennet). Fresh samples of these fruits were collected from three public markets located in the Rayong Districts of Wang Chan, Klang and Mueang. Market locations where samples were collected: Wang Chan is located at 12°57′35″ North latitude and 101°30′12″ East longitude, Klang is located at 12°46′48″ North latitude and 101°39′5″ East longitude, and Mueang is located at 12°38′46″ North latitude and 101°20′49″ East longitude (Figure 1). In this work, the identity of the three markets were concealed by using the pseudonyms market A, market B, and market C. Based on the sampling methods recommended for the determination of pesticide residues (FAO/WHO, 1999; Ministry of Agriculture and Cooperatives, 2008), fruits were classified using the average weight of each fruit type. Thus, three groups of fruit type were defined as: (1) average weight per fruit less than 25 g, (2) average weight per fruit 25-250 g, and (3) average weight per fruit greater than 250 g. Samples for analysis [one kilogram (or ten fruits) (for Groups 1 and 2); two kilograms (or five fruits) (for Group 3)] of each fruit type were randomly collected from different sellers at each market. All samples were kept in clean, zip-lock polythene bags and transported to the Mahidol University laboratory within 48 h.

2.2 Sample preparation

Samples were washed with deionized distilled water. Then edible parts of the fruits were collected, cut into small pieces, and dried in a hot air oven at 80ºC for 24 h (Islam and Hoque, 2014). These samples were weighed before and after drying. The dried samples were powdered by mortar, collected in polythene screw cap tubes and stored at 4ºC until subsequent digestion.

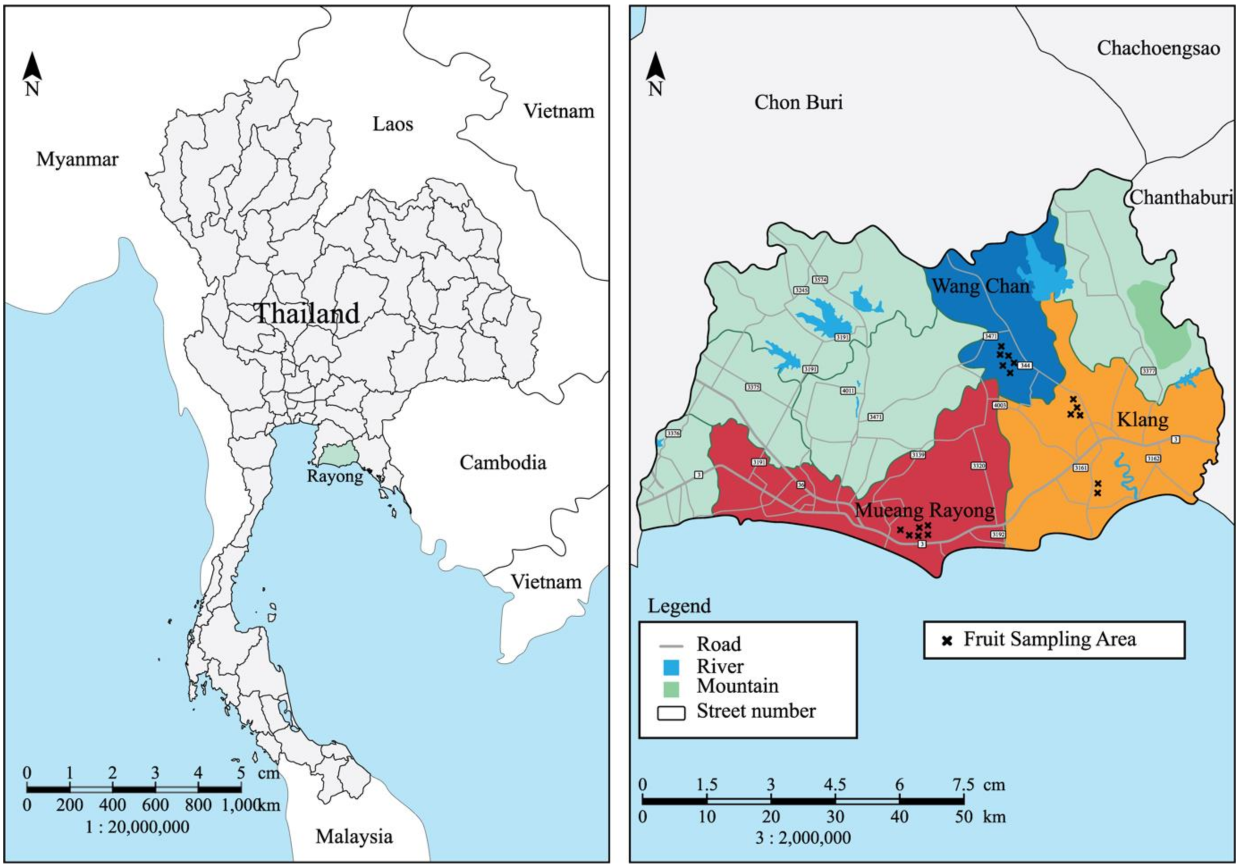

Figure 1. Map showing location of Rayong Province, Thailand (Left), and of study areas within Rayong (Right) where fruits were sampled (in Wang Chan, Klang and Mueang Districts).

2.3 Reagents and materials

Analytical reagents, namely, hydrochloric acid (HCl), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), and stannous chloride ($SnCl_2$) were purchased from Merck (Darmstadt, Germany). A mercury standard (1,000 µg/mL) was purchased from SCP Science (Montreal, QC, Canada), while an ICP multi-element calibration standard of Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Ti, U, V, and Zn (10 mg/mL), and internal calibration standard solutions of Bi, Ge, In, Li, Sc, Tb, and Y (10 mg/mL), were purchased from Perkin Elmer (Waltham, MA, USA). Milli-Q water was used to prepare all stock solutions. Nitric acid and hydrogen peroxide were used for digestion of the dried samples. $SnCl_2$ and HCl were the reducing agents for Hg analyses. The calibration curves and quality control analyses for As, Cd, Cu, Pb, and Zn were prepared by multi-element and internal calibration standard solutions, respectively. All standards and sample solutions were diluted with 1% (v/v) nitric acid solution in Milli-Q water before analysis.

2.4 Hg analysis

A cold vapor-atomic absorption spectrophotometer (Flow Injection Mercury Systems 100 and 400; FIMS series; PerkinElmer) was used for Hg analysis. Sample solutions (500 µL each) were prepared in a mixture of 1.1% (v/v) $SnCl_2$ and 3% (v/v) HCl. The prepared samples were pumped through the reactor with the aid of a peristaltic pump. Then, elemental mercury vapor was generated and entered into a quartz cell for analysis of Hg. A Hg standard curve was established by standard Hg solutions at concentrations of 5, 10, and 20 µg/L. To confirm that the CV-AAS system was working accurately, internal quality control of Hg based on standard Hg solutions (2 and 15 µg/L) were run with every 10 samples. The percentage relative standard deviation (%RSD) value was maintained in the range of 10% to verify precision according to previous research that the acceptable values of RSD for the level analyte of 10 µg/L is 32% (González and Herrador, 2007). In case of Hg analysis, maximum absorbance was obtained by adjusting the Cathode lamps at 253.7 nm, then the absorbance value was converted to a concentration of Hg (with units of mg/kg). Finally, concentration values were compared with maximum permissible limits to detect contamination in fruit samples.

2.5 As, Cd, Cu, Pb, and Zn analyses

An inductively coupled plasma-mass spectrometer (NexION 300 ICP-MS) was used for As, Cd, Cu, Pb, and Zn analyses. Based on NexION® Software Reference Guide, version 1.3, for ICP-MS Instrument Control (PerkinElmer, CT, USA) (Bass and Jones, 2010), standard curves were established using multi-element standard solutions at concentrations of 25, 50, 75, and 100 µg/L. The internal standard solution contained 10 mg/L of Bi, Ge, In, Sc, Li, Tb, and Y. Standards and digested sample solutions were prepared in 1% (v/v) HNO_3. The optimized conditions for As, Cd, Cu, Pb, and Zn analyses were 1.05 L/min of nebulizer gas flow, 1.35 L/min of auxiliary gas flow, 18 L/min of plasma gas flow, and 1,600 W of radio-frequency (RF) in an ICP system. The readings were taken from the equipment as µg/L and then the results were converted to mg/kg (the actual concentration of heavy metal in a sample) using Equation (1).

$$C_i = 0.1 \times A \times \frac{W_D}{W_W} \qquad (1)$$

Where; C_i is the concentration of heavy metal in a sample (mg/kg). A is the concentration of the heavy metal in digested solution (µg/L). W_D is dry weight of the sample (g) and W_w is its wet weight (g). Similar to Hg measurements, concentrations were compared with the appropriate maximum permissible limits.

2.6 Validation and quality control

For validation of the quantitative analyses of heavy metals in fruit samples and their aqueous extracts, evaluation of multiple parameters was performed. The limit of detection (LOD) and limit of quantification (LOQ) were obtained using blank samples (for ICP-MS) and a calibration approach (for CV-AAS) (Wenzl et al., 2016). Moreover, linear range, accuracy, repeatability, and reproducibility (precision) were investigated. To monitor reliability of the results, internal quality control was conducted every 10 samples. Average recoveries were determined for the different heavy metals. In addition, appropriate quality assurance procedures and precautions were taken and all samples were handled carefully to avoid cross-contamination.

2.7 Statistical data analysis

Statistical analyses were performed using SPSS Statistical Package, version 18 (SPSS, Chicago, IL, USA) to assess the influence of sources of variance (fruit type and location) on each heavy metal. Data from each heavy metal in the six fruit types from the three different local markets were included. Descriptive statistics and one-way ANOVA tests were performed. Post hoc comparisons using Tukey HSD test were used to determine differences among the heavy metal concentrations and fruit types. Statistical significance was defined at the 95% confidence level ($*p < 0.05$).

2.8 Health risk assessment

In this study, to assess the human health risks for non-carcinogenic and carcinogenic metals associated with fruit consumption, four approaches were used: (1) estimated daily intake (µg/kg bw/day), (2) target hazard quotient, (3) non-carcinogenic hazard index or total target hazard quotient, and (4) carcinogenic risk.

2.8.1 Estimated daily intake

The estimated daily intake (EDI) of heavy metals was calculated as follows:

$$EDI = \frac{C_i \times F_{IR}}{W_{AB}} \qquad (2)$$

Where; C_i is the concentration of a heavy metal in fruit (mg/kg), F_{IR} is the average daily ingestion rate (g/day) of fruit, and W_{AB} is average body weight (kg). Based on the Thailand National Health Examination Survey (Satheannoppakao et al., 2009), the average daily consumption of durian and jackfruit is 116.8 g/person/day. Based on WHO data, the average daily consumption of pineapple is 9.75 g/person/day, and the average daily consumption of stone fruits (such as mangosteen, rambutan, and long kong) is 7.3 g/person/day (WHO, 2003). Average body weights in the Thai population are 68.5±12.1 kg for males and 54.5±9.8 for females (Lim et al., 2009).

2.8.2 Tolerable daily intake

Tolerable daily intake (TDI) or provisional tolerable daily intake (PTDI) are estimates of the amount of a substance in food that can be taken daily over a lifetime without significant risk to health

(Hashemi et al., 2019). The EDI values in the present study were compared with TDI or PTDI for each heavy metal. Table 1 shows the current provisional tolerable weekly intake (PTWI) or provisional tolerable monthly intake (PTMI) values for Cd, Cu, Hg, Pb, and Zn, and the lower limit of the benchmark dose ($BDML_{0.5}$) value for As based on the Codex Alimentarius (FAO/WHO, 2018) and the calculated TDI values based on PTWI, PTMI, or $BDML_{0.5}$.

Table 1. Provisional tolerable weekly/monthly intake (PTWI /PTMI) and calculated TDI based on the PTWI/PTMI (FAO/WHO, 2018; Mohamed et al., 2019; Bamuwamye et al., 2015)

Heavy metal	PTWI or PTMI (mg/kg bw)	TDI value (mg/kg bw)
As	NA	$0.003^{a,b}$
Cd	0.025 (PTMI)	0.00083^{b}
Cu	3.5 (PTWI)	0.5^{c}
Hg	0.0016 (PTWI)	0.00023^{b}
Pb	NA	NA^{b}
Zn	7 (PTWI)	1^{c}

NA: not applicable; [a]Based on Joint FAO/WHO Expert Committee on Food Additives (JECFA) (FAO/WHO, 2018); [b]Based on Codex Alimentarius International Food Standard (FAO/WHO, 2019); [c]Based on Joint FAO/WHO Expert Committee on Food Additives (JECFA) (FAO/WHO, 1982)

2.8.3 Target hazard quotient

Target hazard quotient (THQ) is a complex parameter derived from the ratio between the reference dose (R_{FD}) and estimated dose of a contaminant, to estimate the potential health risk associated with chronic exposure to that contaminant. It is calculated as follows (Ogwok et al., 2014):

$$THQ = \left(\frac{(E_F \times E_D \times F_{IR} \times C)}{(R_{FD} \times W_{AB} \times T_A)}\right) \times 10^{-3} \quad (3)$$

Where; E_F is the frequency of exposure from consumption of heavy metal contaminated fruits (365 days/year), E_D is the duration of human exposure or the average lifetime of humans (71.8 years for males and 78.6 years for females) (Institute for Population and Social Research, 2016), F_{IR} is the average daily ingestion rate (g/day) of fruit, C is the concentration of a heavy metal in fruits (mg/kg), R_{FD} is the oral reference dose (mg/kg/day) which indicates the daily exposure to which humans can be exposed continually over a lifetime without appreciable risk of deleterious effects, R_{FD} (based on USEPA and CalEPA) for As, Cd, Cu, Hg, Pb, and Zn are 3.0×10^{-4} (IRIS, 2022), 1.0×10^{-3} (IRIS, 2022; Harmanescu et al., 2011), 4.0×10^{-2} (Ogwok et al., 2014; Harmanescu et al., 2011), 1.6×10^{-4} (Zeng et al., 2015), 3.5×10^{-3} (Harmanescu et al., 2011), and 0.3 (IRIS, 2022; Harmanescu et al., 2011) mg/kg/day, respectively, W_{AB} is average body weight which for Thais is 68.5±12.1 kg for males and 54.5±9.8 for females (Lim et al., 2009), T_A is the average time of human exposure to non-carcinogens (365 days/year × 70 years), and 10^{-3} is the unit conversion factor. In case of THQ<1, adverse effects are unlikely to occur; whereas, if THQ≥1, there is a high risk that the toxin induces adverse effects over a lifetime of exposure (Song et al., 2009; Zeng et al., 2015).

2.8.4 Non-carcinogenic hazard index or total target hazard quotient (TTHQ)

The hazard index (HI) was calculated for multiple heavy metals to estimate the total potential non-carcinogenic health impact on the human body caused by the combined exposure to them (Mohammadi et al., 2019). The HI is determined as the sum of all THQs calculated for individual heavy metals using Equation (4):

$$\text{Total THQ (HI)} = \sum_{k=1}^{n} \begin{matrix} THQ = THQ_{As} + THQ_{Cd} + THQ_{Cu} \\ +THQ_{Hg} + THQ_{Pb} + THQ_{Zn} \end{matrix} \quad (4)$$

When; HI<1, chronic risks are unlikely; whereas when HI≥1, chronic non-carcinogenic risks are likely (Cao et al., 2015).

2.8.5 Carcinogenic risk

The carcinogenic risk (CR) is calculated as an estimation of the incremental probability of an individual developing cancer as a result of exposure to a potential carcinogen. According to the International Agency for Research on Cancer, As and Cd are categorized in Group 1 carcinogens: chemicals which are definite human carcinogens; Pb is categorized in Group 2B: chemicals which are possible human carcinogens. CR, defined as the risk generated by a lifetime of average exposure to carcinogenic chemicals (Zeng et al., 2015), is calculated using the cancer slope factor (CSF). In the present study, the CR values due to As, Cd, and Pb were each calculated using Equation (5):

$$CR = \left[\frac{E_F \times E_D \times F_{IR} \times C \times CSF}{W_{AB} \times T_A}\right] \quad (5)$$

Where; E_F is the frequency of exposure from consumption of heavy metal-contaminated fruits (365-day/year), E_D is the duration of exposure or the average lifetime of humans, F_{IR} is the average daily ingestion rate (kg/day) of fruit, C is the concentration of heavy metals in fruits (mg/kg), CSF is the cancer slope factor which is provided by IRIS and CALEPA [1.50 mg/kg/day for As (Hashemi et al., 2019; IRIS, 2022); 15 mg/kg/day for Cd (Zeng et al., 2015); 0.0085 mg/kg/day for Pb (Hashemi et al., 2019)], W_{AB} is average body weight, for adult Thais, this is 68.5±12.1 kg for males and 54.5±9.8 for females (Lim et al., 2009), and T_A is the average time of human exposure to non-carcinogens (365 days/year × 70 years).

When multiple carcinogenic elements were present, the total carcinogenic risk (CR_{Total}) (Zeng et al., 2015) was described using Equation (6):

$$CR_{Total} = \sum CR \quad (6)$$

Where; CR is the carcinogenic risk associated with each heavy metal.

Based on the USEPA, a CR value of 1×10^{-6} is considered the point of excess carcinogenic risk. This value indicates a probability of 1/1,000,000 for an individual to develop cancer (based on g/day for 70 years). For each heavy metal, a CR value less than 1×10^{-6} is considered insignificant and cancer risk can be neglected; a CR value above 1×10^{-4} is considered as significant and that there is a cancer risk. CR_{Total} values of 1.0×10^{-6} to 1.0×10^{-4} are considered acceptable (Cao et al., 2015); we chose a CR_{Total} of 1.0×10^{-5} as the cut-off of acceptable levels as did by Mohammadi et al. (2019).

3. RESULTS AND DISCUSSION

In this study, levels of As, Cd, Cu, Pb, and Zn were determined by ICP-MS, and of Hg by CV-AAS. The analytical performance of these methods was investigated and the results are shown in Table 2. A calibration curve was established for each heavy metal (data not shown). Plots of intensity and absorbance against spiked standards were linear and in the range of 0.01-100 µg/L and 0.001-0.040 mg/kg for ICP-MS and CV-AAS, respectively. Established calibration curves had correlation coefficients of 0.9979-0.9997. Limits of detection and quantification were 0.001-0.440 and 0.005-0.500 mg/kg, respectively. The recovery of different heavy metals was within the range of 70-120%, with %RSD ≤ 20% consistent with SANTE/11813/2017 documentation (European Commission, 2017).

3.1 Heavy metal concentrations

Concentrations of heavy metals contaminating the fruits collected from three markets in Rayong, namely market A, market B, and market C, are presented in Table 3. The metals varied in concentration among the different fruits. A high content of essential micronutrients (Cu and Zn) was found, ranging from 0.2926 to 6.7095 mg/kg. Concentrations of toxic metals (As, Cd, Hg, and Pb) ranged from 0.0004 to 0.4625 mg/kg. Additionally, the concentrations of individual heavy metals were investigated. The order of metal concentrations was: for As, jackfruit > durian > mangosteen > long kong > pineapple > rambutan; for Cd, mongosteen > jackfruit > durian > rambutan > long kong > pineapple; for Cu, jackfruit > durian > rambutan > mangosteen > long kong > pineapple; for Hg, jackfruit > durian > pineapple > mangosteen/rambutan > long kong; for Pb, long kong > jackfruit > durian > rambutan > pineapple > mangosteen; for Zn, jackfruit > durian > rambutan > long kong > mangosteen > pineapple.

The level of Pb in 16.7% of fruit samples exceeded the permissible level of contamination (0.1 mg/kg) [durian in market B (0.1427±0.0635 mg/kg), jackfruit in market B (0.2949±0.0763 mg/kg), and long kong in market A (0.4625±0.0604 mg/kg)]. Based on these results, consumption of fruits collected in these areas should raise concern for Pb contamination. Its presence might be due to phosphate fertilizer application as described in reports from Cakmak et al. (2010) and Satachon et al. (2019), or derived from the heavy metal-related industries which contribute to cultivated area contamination (via soil and water) (Kumar et al., 2020). Several studies on heavy metal contamination have been reported from Thai provinces where many industrial estates are located, for example Pathumthani and Ayutthaya Provinces (Jankeaw et al., 2015; Kladsomboon et al., 2020). Given the lead results from this study in Rayong, concentrations should be periodically monitored and actions taken to prevent potential harm. Moreover, more in-depth studies should be conducted to inform future public health strategies.

Cadmium was also found in fruit samples collected in this study. Although the concentrations of Cd did not exceed permissible limits, accumulation of Cd is an important issue and needs to be monitored due to its carcinogenic potential. There are updates of

Table 2. Coefficient of determination (R^2), calibration range, %recovery, relative standard deviations (%RSD), LOD, and LOQ of ICP-MS and CV-AAS in analyses of fruit samples

Heavy metals	R^2 value	Calibration range (μg/L)	Calibration range (mg/kg)	%Recovery (Mean±SD)	%RSD	LOD (mg/kg)	LOQ (mg/kg)
As*	0.9992	0.55-100	0.055-10	106.00±0.34	3.2020	0.055	0.010
Cd*	0.9986	0.01-100	0.001-10	104.70±0.69	6.6186	0.001	0.010
Cu*	0.9996	4.40-100	0.440-10	99.97±0.04	0.3530	0.440	0.500
Hg**	0.9997	0.01-0.40	0.001-0.04	93.5000±0.0007	3.7813	0.001	0.005
Pb*	0.9993	0.01-100	0.001-10	106.55±0.16	1.5264	0.001	0.010
Zn*	0.9979	2.40-100	0.240-10	106.50±0.13	1.1951	0.240	0.270

* measured by ICP-MS; ** measured by CV-AAS

guidelines for soil Cd concentration (Six and Smolders, 2014) aimed to avoid net Cd accumulation (Smolders and Six, 2013). Based on our results, Cd concentrations in fruits were low enough for safe consumption.

Arsenic and mercury were found in small amounts in sampled fruits. As and Hg contamination of fruits may occur through the absorption of these heavy metals after pesticide application and contamination of cultivated areas as described by Li et al. (2016). For example, As-containing pesticides (with lead arsenate, copper arsenate and calcium arsenate) were extensively used on some fruits to control cattle ticks and pests, leading to accumulation in plant tissue (Madejón et al., 2006). Hg is a toxic metal which has effects on the nervous, digestive and kidney systems. It is considered by WHO as one of the top ten chemicals of major public health concern (WHO, 2020). Similar to the sources of Pb contamination, Hg often enters the environment via pesticide application and emission from heavy metal-related industries (Turull et al., 2018; Li et al., 2017). A report from Ecological Alert and Recovery-Thailand (EARTH) warned of Hg contamination in industrial sites in Rayong Province (EARTH, 2016) and its spread to farmland and orchards with potential contamination of fruits. However, concentrations of mercury in our study samples were below the maximum permissible limit from the Ministry of Public Health, Thailand, suggesting that fruit from this study area are safe for consumption.

Copper and zinc are essential micronutrients for plant growth, participating in several processes including photosynthetic electron transport, cell wall and nitrogen metabolism, and protein regulation (Shabbir et al., 2020; Liščáková et al., 2022). However, in agriculture, Cu is also considered an antifungal agent usually used as copper sulphate and copper oxychloride. Extensive application of this agent can lead to Cu release into the environment (Seeda et al., 2020). In this study, results demonstrated that all fruit samples were rich in Cu and Zn, especially the jackfruit and durian. However, the concentrations of Cu and Zn were less than the permissible limits and the fruits considered safe for consumption.

According to the statistical plan, one-way analysis of variance was used to compare heavy metal (As, Cd, Cu, Hg, Pb, and Zn) residues in the fruits collected in each location (market A, B, and C).

Table 3. Mean concentrations (mg/kg)±S.D. of heavy metals in Rayong fruits and their maximum permissible limits

Samples	Market	As	Cd	Cu	Hg	Pb	Zn
Durian	A	0.0183±0.0009	0.0078±0.0016	0.9276±0.0470	0.0026±0.0003	0.0944±0.0023	2.1634±0.2499
	B	0.0049±0.0000	0.0112±0.0002	2.2244±0.0238	0.0045±0.0009	0.1427±0.0635	2.0812±0.0596
	C	0.0177±0.0016	0.0062±0.0002	1.7258±0.1296	0.0058±0.0006	0.0611±0.0053	2.5706±0.2659
Jackfruit	A	0.0038±0.0001	0.0060±0.0003	2.4548±0.0364	0.0046±0.0002	0.0869±0.0179	1.8466±0.0024
	B	0.0241±0.0013	0.0274±0.0046	5.5860±0.0043	0.0144±0.0042	0.2949±0.0763	6.7095±1.3070
	C	0.0142±0.0007	0.0035±0.0003	1.9873±0.0914	0.0013±0.0001	0.0213±0.0021	1.3915±0.1091
Mangosteen	A	0.0102±0.0010	0.0073±0.0007	1.2953±0.2125	0.0023±0.0001	0.0096±0.0002	0.7796±0.0436
	B	0.0016±0.0001	0.0119±0.0000	0.9383±0.0361	0.0023±0.0001	0.0333±0.0086	0.9097±0.0111
	C	0.0043±0.0003	0.0192±0.0021	0.5860±0.0520	0.0020±0.0001	0.0078±0.0004	0.7260±0.0735
Pineapple	A	0.0045±0.0004	0.0005±0.0001	0.6374±0.0100	0.0024±0.0001	0.0273±0.0078	0.7659±0.0265
	B	0.0023±0.0002	0.0004±0.0000	0.2926±0.0036	0.0020±0.0002	0.0113±0.0007	0.3325±0.0044
	C	0.0041±0.0012	0.0011±0.0001	0.5043±0.1894	0.0026±0.0001	0.0173±0.0051	0.9092±0.2915
Rambutan	A	0.0036±0.0020	0.0033±0.0006	1.2471±0.1288	0.0029±0.0003	0.0289±0.0024	2.2017±0.2091
	B	0.0019±0.0001	0.0026±0.0002	1.0895±0.0910	0.0014±0.0010	0.0272±0.0032	1.3416±0.0877
	C	0.0037±0.0005	0.0033±0.0013	0.8838±0.1167	0.0023±0.0003	0.0566±0.0608	1.1674±0.1796
Long kong	A	0.0046±0.0004	0.0014±0.0001	1.5142±0.2333	0.0008±0.0002	0.4625±0.0604	1.2572±0.1891
	B	0.0035±0.0001	0.0019±0.0000	0.6639±0.0373	0.0010±0.0001	0.0097±0.0002	1.0441±0.0514
	C	0.0036±0.0001	0.0021±0.0003	0.4628±0.0165	0.0020±0.0004	0.0188±0.0019	0.9153±0.0069
Maximum permissible limits (mg/kg)		2[a]	0.05[a,b]	20[c]	0.02[a]	0.1[a,b]	99.4[d]

[a]Based on Standard for Contaminants in Food (MoPH, 2020).
[b]Based on Codex Alimentarius International Food Standard (FAO/WHO, 2019).
[c]Based on EU Pesticides database (EU, 2022).
[d]Based on Joint FAO/WHO Joint Expert Committee on Food Additives (JECFA) (FAO/WHO, 1996; Mensah et al., 2009).

The analyses revealed that there were no statistically significant differences of the As [F(2.33=0.167), p=0.847], Cd [F(2.33=1.341), p=0.276], Cu [F(2.33=1.272), p=0.294], Hg [F(2.33=1.203), p=0.313], Pb [F(2.33=1.748), p=0.190], nor Zn [F(2.33=1.000), p=0.379] levels among locations at the 95% confidence level. However, concentrations of metals were significantly different with regard to type of fruit. Significant differences of As [F(5.30=6.721), p^*=0.000], Cd [F(5.30=5.863), p^*=0.001], Cu [F(5.30=9.825), p^*=0.000], Hg [F(5.30=3.112), p^*=0.022], and Zn [F(5.30=4.787), p^*=0.002] were found, while differences of Pb [F(5.30=1.903), p=0.123] were not significant.

To determine the source of differences, post hoc tests were used to discriminate and explain heavy metal concentrations among the six fruit types (comparing each to the other five fruit types for each heavy metal). The analyses revealed statistically significant differences among the heavy metal concentrations. In detail, there were statistically significant differences among seven pairs (durian and pineapple, durian and rambutan, durian and long kong, jackfruit and pineapple, jackfruit and rambutan, jackfruit and long kong, jackfruit and mangosteen) for As, five pairs (jackfruit and pineapple, jackfruit and long kong, pineapple and mangosteen, rambutan and mangosteen, long kong and mangosteen) for Cd, five pairs (durian and jackfruit, jackfruit and pineapple, jackfruit and rambutan, jackfruit and long kong, jackfruit and mangosteen) for Cu, one pair (jackfruit and long kong) for Hg, and three pairs (jackfruit and pineapple, jackfruit and long kong, jackfruit and mangosteen) for Zn.

However, the different concentrations of detected metals in each fruit type might be due to differing causes, such as physiology of the fruits, status of heavy metal contamination, proximity to industrial areas, type of industrial activity, agricultural activities (for example, fertilizer application), transportation, sample storage and preparation for assay (Taiwo et al., 2022; Ghasemidehkordi et al., 2018).

Given the results of this study, long- term consumption of some fruit posed the potential for adverse health effects. Therefore, health risk assessments were carried out in this study area.

3.2 Risk assessments of heavy metals

To assess the human health risks from both non-carcinogenic and carcinogenic metals associated with fruit consumption, four approaches were utilized: (1) estimated daily intake, (2) target hazard quotient, (3) non-carcinogenic hazard index or total target hazard quotient, and (4) carcinogenic risk.

A dietary exposure approach was used for evaluation of ingestion levels of nutrients and even contaminants. Estimated daily intake of individual heavy metals through fruit consumption are shown in Table 4. High EDI values were found for jackfruit and durian with all heavy metals, for both males and females. The EDIs were, in descending order, Zn>Cu>Pb>As>Cd>Hg for both genders for market A and C, and Zn>Cu>Pb>Cd>As>Hg for both genders in market B. These results were in agreement with a 2006 report from Egypt (Radwan and Salama, 2006) that Cu and Zn are the metals most frequently found in fruits and vegetables. Moreover, these EDI values were below the maximum tolerable daily intake (MTDI) and calculated TDI from PTWI/PTMI as recommended in the FAO/WHO guideline (see in Table 1). Thus, there appeared to be no or little possibility of adverse health effects from Cu or Zn through fruit consumption by either gender.

Target health quotient, non-carcinogenic hazard index, and carcinogenic risk were also used for estimation of the potential health risks associated with chronic exposure to heavy metals. Values were calculated using the heavy metal concentrations found in fruits from the three sampled Rayong markets and the estimated average fruit consumption by the local population. The THQ and HI values, obtained using fruit samples, are shown in Tables 5 and 6 for males and females, respectively. The average THQs of each heavy metal through fruit ingestion by males were Cu (0.2269), As (0.1682), Hg (0.1280), Pb (0.1244), Cd (0.0384), and Zn (0.0341). Results were similar for females: Cu (0.3122), As (0.2315), Hg (0.1761), Pb (0.1712), Cd (0.0528), and Zn (0.0469). All calculated THQs were < 1, suggesting that adverse effects would be unlikely. The average HI values of the six heavy metals for males and females were 0.7202 and 0.9909, respectively. Since these HI values were less than 1, chronic health risks were unlikely to occur. However, the risk was somewhat higher in females due to longer duration of exposure than in males. In addition, HI values were estimated for each market. The calculated HI values were, in descending order, market B (1.0797) > market A (0.5439) > market C (0.5370) for males, and market B (1.4855) > market A (0.7484) > market C (0.7389) for females. It was the high

Table 4. Estimated daily intake (μg/kg bw/day) and tolerable daily intake of heavy metals

Fruit	FIR (g/day)	Market	Male (BW=68.5 kg)						Female (BW=54.5 kg)					
			As	Cd	Cu	Hg	Pb	Zn	As	Cd	Cu	Hg	Pb	Zn
Durian	116.8	A	0.0313	0.0133	1.5818	0.0045	0.1610	3.6889	0.0393	0.0168	1.9881	0.0056	0.2024	4.6366
		B	0.0084	0.0191	3.7928	0.0077	0.2434	3.5487	0.0106	0.0240	4.7671	0.0096	0.3059	4.4604
		C	0.0302	0.0106	2.9427	0.0099	0.1042	4.3831	0.0379	0.0133	3.6986	0.0125	0.1309	5.5091
Jackfruit	116.8	A	0.0065	0.0103	4.1857	0.0078	0.1481	3.1487	0.0082	0.0130	5.2609	0.0099	0.1862	3.9575
		B	0.0412	0.0467	9.5248	0.0246	0.5028	11.440	0.0518	0.0588	11.971	0.0309	0.6320	14.379
		C	0.0243	0.0059	3.3885	0.0023	0.0363	2.3727	0.0306	0.0075	4.2590	0.0028	0.0456	2.9822
Mangosteen	7.3	A	0.0010	0.0007	0.1380	0.0002	0.0010	0.0830	0.0013	0.0009	0.1735	0.0003	0.0012	0.1044
		B	0.0001	0.0012	0.1000	0.0002	0.0035	0.0969	0.0002	0.0016	0.1256	0.0003	0.0044	0.1218
		C	0.0004	0.0020	0.0624	0.0002	0.0008	0.0773	0.0005	0.0025	0.0784	0.0002	0.0010	0.0972
Pineapple	9.75	A	0.0006	0.0000	0.0907	0.0003	0.0038	0.1090	0.0008	0.0001	0.1140	0.0004	0.0048	0.1370
		B	0.0003	0.0000	0.0416	0.0002	0.0016	0.0473	0.0004	0.0000	0.0523	0.0003	0.0020	0.0594
		C	0.0005	0.0001	0.0717	0.0003	0.0024	0.1294	0.0007	0.0002	0.0902	0.0004	0.0031	0.1626
Rambutan	7.3	A	0.0003	0.0003	0.1329	0.0003	0.0030	0.2346	0.0004	0.0004	0.1670	0.0003	0.0038	0.2949
		B	0.0002	0.0002	0.1161	0.0001	0.0029	0.1429	0.0002	0.0003	0.1459	0.0001	0.0036	0.1797
		C	0.0003	0.0003	0.0941	0.0002	0.0060	0.1244	0.0005	0.0004	0.1183	0.0003	0.0075	0.1563
Long Kong	7.3	A	0.0004	0.0001	0.1613	0.0000	0.0492	0.1339	0.0006	0.0001	0.2028	0.0001	0.0619	0.1683
		B	0.0003	0.0002	0.0707	0.0001	0.0010	0.1112	0.0004	0.0002	0.0889	0.0001	0.0013	0.1398
		C	0.0003	0.0002	0.0493	0.0002	0.0020	0.0975	0.0004	0.0002	0.0619	0.0002	0.0025	0.1226
Sum of EDI (All 6 fruits)		A	0.0404	0.0251	6.2906	0.0133	0.3665	7.3984	0.0508	0.0315	7.9065	0.0168	0.4606	9.2989
		B	0.0507	0.0677	13.646	0.0331	0.7553	15.387	0.0638	0.0851	17.151	0.0416	0.9494	19.340
		C	0.0564	0.0194	6.6090	0.0133	0.1518	7.1846	0.0709	0.0244	8.3067	0.0167	0.1908	9.0302
Calculated TDI			3[a,b]	0.83[b]	500	0.23[b]	NA[b]	1,000	3[a,b]	0.83[b]	500	0.23[b]	NA[b]	1,000
Maximum tolerable daily intake (MTDI) (Hashemi et al., 2019; FAO/WHO, 2002)			1.8	0.8	166.7	1.3	3	300	1.8	0.8	166.7	1.3	3	300

[a]Based on Joint FAO/WHO Expert Committee on Food Additives (JECFA) (FAO/WHO, 2018)
[b]Based on Codex Alimentarius International Food Standard (FAO/WHO, 2019)

Table 5. Target hazard quotient and non-carcinogenic hazard index by metal and fruit in males

Fruit	Market	THQ of individual heavy metals (For 68.5 kg male)						∑ THQ HI	HI Average
		As	Cd	Cu	Hg	Pb	Zn		
Durian	A	0.1070	0.0137	0.0405	0.0289	0.0471	0.0126	0.2500	0.2760
	B	0.0288	0.0196	0.0972	0.0494	0.0713	0.0121	0.2786	
	C	0.1033	0.0109	0.0754	0.0640	0.0305	0.0149	0.2992	
	Average	0.0797	0.0147	0.0710	0.0474	0.0496	0.0132		
Jackfruit	A	0.0223	0.0106	0.1073	0.0504	0.0434	0.0107	0.2449	0.4108
	B	0.1410	0.0479	0.2442	0.1579	0.1473	0.0391	0.7777	
	C	0.0833	0.0061	0.0868	0.0147	0.0106	0.0081	0.2098	
	Average	0.0822	0.0215	0.1461	0.0744	0.0671	0.0193		
Mangosteen	A	0.0037	0.0008	0.0035	0.0015	0.0003	0.0002	0.0102	0.0083
	B	0.0006	0.0013	0.0025	0.0016	0.0010	0.0003	0.0074	
	C	0.0015	0.0021	0.0016	0.0014	0.0002	0.0002	0.0072	
	Average	0.0019	0.0014	0.0025	0.0015	0.0005	0.0002		
Pineapple	A	0.0022	0.0000	0.0023	0.0022	0.0011	0.0003	0.0083	0.0069
	B	0.0011	0.0000	0.0010	0.0018	0.0004	0.0001	0.0047	
	C	0.0020	0.0001	0.0018	0.0024	0.0007	0.0004	0.0076	
	Average	0.0018	0.0001	0.0017	0.0021	0.0007	0.0003		
Rambutan	A	0.0013	0.0003	0.0034	0.0019	0.0009	0.0008	0.0088	0.0076
	B	0.0007	0.0002	0.0029	0.0009	0.0008	0.0004	0.0062	
	C	0.0013	0.0003	0.0024	0.0015	0.0017	0.0004	0.0079	
	Average	0.0011	0.0003	0.0029	0.0015	0.0011	0.0005		
Long kong	A	0.0016	0.0001	0.0041	0.0006	0.0144	0.0004	0.0214	0.0104
	B	0.0012	0.0002	0.0018	0.0007	0.0003	0.0003	0.0047	
	C	0.0013	0.0002	0.0012	0.0013	0.0005	0.0003	0.0051	
	Average	0.0014	0.0002	0.0024	0.0009	0.0051	0.0003		
Calculated THQ	A	0.1383	0.0257	0.1613	0.0858	0.1074	0.0252	0.5439	0.7202
	B	0.1736	0.0695	0.3499	0.2126	0.2213	0.0526	1.0797	
	C	0.1929	0.0199	0.1694	0.0856	0.0445	0.0245	0.5370	
Average THQ		0.1682	0.0384	0.2269	0.1280	0.1244	0.0341		

Table 6. Target hazard quotient and non-carcinogenic hazard index by metal and fruit in females

Fruit	Market	THQ of individual heavy metals (For 54.5 kg female)						∑ THQ HI	HI average
		As	Cd	Cu	Hg	Pb	Zn		
Durian	A	0.1472	0.0188	0.0558	0.0398	0.0649	0.0173	0.3440	0.3797
	B	0.0396	0.0270	0.1338	0.0680	0.0981	0.0166	0.3834	
	C	0.1421	0.0150	0.1038	0.0881	0.0420	0.0206	0.4117	
	Average	0.1097	0.0203	0.0978	0.0653	0.0683	0.0182		
Jackfruit	A	0.0307	0.0146	0.1476	0.0694	0.0597	0.0148	0.3370	0.5652
	B	0.1940	0.0660	0.3360	0.2173	0.2027	0.0538	1.0700	
	C	0.1146	0.0084	0.1195	0.0203	0.0146	0.0111	0.2887	
	Average	0.1131	0.0297	0.2011	0.1023	0.0923	0.0265		
Mangosteen	A	0.0051	0.0011	0.0048	0.0021	0.0004	0.0003	0.0140	0.0114
	B	0.0008	0.0018	0.0035	0.0022	0.0014	0.0004	0.0103	
	C	0.0021	0.0028	0.0022	0.0019	0.0003	0.0003	0.0099	
	Average	0.0027	0.0019	0.0035	0.0021	0.0007	0.0004		
Pineapple	A	0.0030	0.0001	0.0032	0.0031	0.0015	0.0005	0.0115	0.0095
	B	0.0015	0.0000	0.0014	0.0025	0.0006	0.0002	0.0065	
	C	0.0028	0.0002	0.0025	0.0033	0.0009	0.0006	0.0105	
	Average	0.0024	0.0001	0.0024	0.0030	0.0010	0.0004		
Rambutan	A	0.0018	0.0005	0.0046	0.0027	0.0012	0.0011	0.0121	0.0105
	B	0.0009	0.0003	0.0040	0.0013	0.0011	0.0006	0.0086	
	C	0.0018	0.0005	0.0033	0.0021	0.0024	0.0005	0.0108	
	Average	0.0015	0.0004	0.0040	0.0020	0.0016	0.0007		
Long kong	A	0.0023	0.0002	0.0056	0.0008	0.0198	0.0006	0.0295	0.0143
	B	0.0017	0.0002	0.0024	0.0010	0.0004	0.0005	0.0065	
	C	0.0018	0.0003	0.0017	0.0018	0.0008	0.0004	0.0070	
	Average	0.0019	0.0002	0.0033	0.0012	0.0070	0.0005		
Calculated THQ	A	0.1902	0.0354	0.2219	0.1181	0.1477	0.0348	0.7484	0.9909
	B	0.2389	0.0956	0.4814	0.2925	0.3045	0.0723	1.4855	
	C	0.2654	0.0274	0.2331	0.1178	0.0612	0.0337	0.7389	
Average THQ		0.2315	0.0528	0.3122	0.1761	0.1712	0.0469		

concentrations of heavy metals (see Table 3) which led to the high HI values. High HI values (>1) indicated a possibility of chronic non-carcinogenic risk to humans in the case of long-term fruit consumption. Therefore, these results can be used in warning farmers to be aware of the heavy metal-contaminated fruits and consumers of the health risk.

3.3 Carcinogenic assessment

As, Cd, and Pb are classified as being carcinogenic by the International Agency for Research on Cancer (IARC, 2018). We therefore calculated and estimated their carcinogenic risk (CR) values. This was assessed based on intake levels and the cancer slope factor (CSF) of the specified heavy metal. The calculated values are shown in Table 7. The average CR values by fruit, in descending order were: jackfruit > durian > mangosteen > pineapple > long kong > rambutan for As; jackfruit > durian > mangosteen > rambutan > long kong > pineapple for Cd; jackfruit > durian > long kong > rambutan > pineapple > mangosteen for Pb (in both males and females). Individual CR values for As, Cd, and Pb in all fruits sampled ranged from 0.007-990.657 ($\times 10^{-6}$), Thus, all CR values were less than 1×10^{-4}, except Cd in durian (all market sites) and jackfruit (market A and B). Of all CR values, 10.2% were higher than the acceptable range. This suggested that prolonged consumption of durian or jackfruit from these areas carried a cancer risk related to cadmium but not to arsenic nor lead.

Total CRs were also estimated using the sum CRs (ΣCR) of As, Cd, and Pb. As shown in Table 7, total CR values were in the range of 1.56×10^{-6} to 1.08×10^{-3}. Total CR values above the acceptable level (1×10^{-5}) were found with durian, jackfruit and mangosteen: 2.58×10^{-4}, 3.62×10^{-4}, and 2.19×10^{-5} for males; 3.56×10^{-4}, 4.99×10^{-4}, and 3.02×10^{-5} for females. These results suggested that there was a carcinogenic risk to consumer health with the long-term consumption of these fruits.

Table 7. Carcinogenic risks associated with local fruit consumption ($\times 10^{-6}$)

Fruits	Market	Male (BW=68.5 kg)			∑ CR	Female (BW=54.5 kg)			∑ CR
		As	Cd	Pb		As	Cd	Pb	
Durian	A	48.158	205.776	1.404	255.339	66.261	283.131	1.931	351.325
	B	12.981	294.576	2.122	309.680	17.861	405.313	2.919	426.094
	C	46.502	163.858	0.908	211.269	63.983	225.454	1.250	290.688
	Average	35.880	221.403	1.478	258.762	49.368	304.633	2.033	356.036
Jackfruit	A	10.047	159.384	1.291	170.723	13.825	219.299	1.777	234.901
	B	63.455	719.997	4.384	787.837	87.309	990.657	6.032	1,083.998
	C	37.486	92.071	0.316	129.875	51.578	126.683	0.435	178.697
	Average	36.996	323.818	1.997	362.812	50.904	445.546	2.748	499.199
Mangosteen	A	1.673	12.075	0.008	13.757	2.303	16.614	0.012	18.929
	B	0.278	19.623	0.030	19.933	0.383	27.000	0.042	27.426
	C	0.712	31.518	0.007	32.238	0.980	43.366	0.009	44.357
	Average	0.888	21.072	0.015	21.976	1.222	28.993	0.021	30.237
Pineapple	A	0.996	1.291	0.033	2.322	1.371	1.777	0.046	3.195
	B	0.516	1.032	0.014	1.562	0.710	1.420	0.019	2.150
	C	0.917	2.595	0.021	3.534	1.261	3.571	0.029	4.862
	Average	0.810	1.639	0.023	2.473	1.114	2.256	0.031	3.402
Rambutan	A	0.602	5.570	0.026	6.199	0.828	7.664	0.036	8.530
	B	0.325	4.338	0.025	4.689	0.447	5.969	0.034	6.451
	C	0.613	5.488	0.052	6.154	0.843	7.551	0.072	8.467
	Average	0.513	5.132	0.034	5.681	0.706	7.061	0.048	7.816
Long Kong	A	0.756	2.381	0.429	3.568	1.040	3.277	0.591	4.909
	B	0.581	3.244	0.009	3.834	0.799	4.463	0.012	5.276
	C	0.593	3.497	0.017	4.107	0.815	4.811	0.024	5.651
	Average	0.643	3.041	0.152	3.836	0.885	4.184	0.209	5.279

4. CONCLUSION

In this study, the levels of heavy metals (As, Cd, Cu, Hg, Pb, and Zn) in fresh fruit samples did not exceed the permissible limits, except for lead in durian (market B), jackfruit (market B), and long kong (market A). No significant differences in heavy metal concentration were found related to sampling location. On the other hand, the levels of As, Cd, Cu, Hg, and Zn were significantly different among fruit types. Based on the THQ calculations, consumption of these fruits in this area was safe from heavy metal accumulation when fruit types were estimated individually. But collectively, consumption of all these fruits was associated with chronic non-carcinogenic risk in some market sites (market B: HI=1.0797 and 1.4855 for males and females, respectively). Carcinogenic risk was highest in relation to cadmium ingestion (average CR value 3.44×10^{-4}), while less so in relation to lead and arsenic. Furthermore, consumption of three of the six fruit types (durian, jackfruit, and mangosteen) carried some carcinogenic risk based on total CR assessment. This study may be helpful in decreasing health risks associated with fruit consumption, encouraging the monitoring of fruits for heavy metals, and informing future remediation strategies.

ACKNOWLEDGEMENTS

This research project is supported by Mahidol University. This research and innovation activity is funded by National Research Council of Thailand (NRCT).

REFERENCES

Bamuwamye M, Ogwok P, Tumuhairwe V. Cancer and non-cancer risks associated with heavy metal exposures from street foods: Evaluation of roasted meats in an urban setting. Journal of Environment Pollution and Human Health 2015;2(3):24-30.

Bass D, Jones D. The determination of trace metals in human urine using the NexION 300 ICP-MS. Atomic Spectroscopy 2010;31(5):165-9.

Big CL, Lacatusu R, Damian F. Heavy metals in soil-plant system around Baia Mare City, Romania. Carpathian Journal of Earth and Environmental Sciences 2012;7(3):219-30.

Cakmak D, Saljnikov E, Mrvic V, Jakovljevic M, Marjanovic Z, Sikiric B, et al. Soil properties and trace elements contents following 40 years of phosphate fertilization. Journal of Environmental Quality 2010;39(2):541-7.

Cao S, Duan X, Zhao X, Wang B, Ma J, Fan D, et al. Health risk assessment of various metal (loid) s via multiple exposure pathways on children living near a typical lead-acid battery plant, China. Environmental Pollution 2015;200:16-23.

Choprathumma C, Thongkam T, Jaiyen C, Tusai T, Apilux A, Kladsomboon S. Determination of toxic heavy metal contaminated in food crops in Nakhon Pathom Province, Thailand. Khon Kaen Agriculture Journal 2019;7(1):83-94.

Dorsey A, Ingerman L, Swarts S. Toxicological Profile for Copper. USA: U.S. Department of Health and Human Services and Agency for Toxic Substances and Disease Registry; 2004.

Dunseith B. Thailand's Eastern Economic Corridor - What You Need to Know [Internet]. 2018 [cited 2022 Aug 23]. Available from: https://www.aseanbriefing.com/news/thailand-eastern-economic-corridor/.

Ecological Alert and Recovery-Thailand (EARTH). Heavy metals in water: Serious pollution concentration found near industrial areas in Thailand [Internet]. 2016 [cited 2021 Jul 16]. Available from: https://english.arnika.org/press-releases/thailand-high-concentration-of-heavy-metals-found-in-water.

European Union (EU). EU pesticides database [Internet]. 2022 [cited 2022 May 21]. Available from: https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/mrls/?event=search.pr.

European Commission. Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed: SANTE/11813/2017. Brussels, Belgium: European Commission; 2017.

Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO). Codex Alimentarius - General Standards for Contaminants and Toxins in Food. Schedule 1: Maximum and Guideline Levels for Contaminants and Toxins in Food. Reference CX-FAC 02/16. Rotterdam, Netherland: Joint FAO/WHO Food Standards Programme, Codex Committee; 2002.

Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO). Codex Alimentarius - General Standard for Contaminants and Toxins in Food and Feed. (Last amended 2019). CODEX STAN. 193-1995. Geneva, Switzerland: Joint FAO/WHO Food Standard Programme, Codex Committee; 2019.

Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO). Diet, Nutrition and the Prevention of Chronic Diseases. Geneva, Switzerland: Joint FAO/WHO Expert Consultation; 2003.

Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO). Evaluation of Certain Food Additives and Contaminants. Geneva, Switzerland: Joint FAO/WHO Expert Committee on Food Additives; 1982.

Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO). Recommended Methods of Sampling for the Determination of Pesticide Residues for Compliance with MRLs (CAC/GL 33-1999). Rome, Italy: Joint FAO/WHO Food standards Programme; 1999.

Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO). Safety Evaluation of Certain Contaminants in Food. Geneva, Switzerland: Joint FAO/WHO Expert Committee on Food Additives; 2011.

Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO). The List of Maximum Levels for Contaminatants and Toxins in Foods. Utrecht, Netherland: Joint FAO/WHO Expert Committee on Food Additives; 2018.

Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO). Toxicological Evaluation of Certain Food Additives and Contaminants in Food/Prepared by the Forty-Fourth Meeting of the Joint FAO/WHO Expert Committee on Food Additives. Rome, Italy: Joint FAO/WHO Expert Committee on Food Additives; 1996.

Ghasemidehkordi B, Malekirad AA, Nazem H, Fazilati M, Salavati H, Shariatifar N, et al. Concentration of lead and mercury in collected vegetables and herbs from Markazi province, Iran: A non-carcinogenic risk assessment. Food and Chemical Toxicology 2018;113:204-10.

González AG, Herrador MÁ. A practical guide to analytical method validation, including measurement uncertainty and accuracy profiles. TrAC Trends in Analytical Chemistry 2007;26(3):227-38.

Harmanescu M, Alda LM, Bordean DM, Gogoasa I, Gergen I. Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area: A case study: Banat County, Romania. Chemistry Central Journal 2011;5(1):1-10.

Hashemi M, Sadeghi A, Saghi M, Aminzare M, Raeisi M, Rezayi M, et al. Health risk assessment for human exposure to trace metals and arsenic via consumption of hen egg collected from largest poultry industry in Iran. Biological Trace Element Research 2019;188(2):485-93.

Hurst R, Hurst S. Fruits and vegetables as functional foods for exercise and inflammation. In: Bioactive Food as Dietary Interventions for Arthritis and Related Inflammatory Diseases. Academic Press; 2012. p. 319-36.

Institute for Population and Social Research. Population of Thailand: Volume 25. Mahidol Population Gazette; 2016.

International Agency for Research on Cancer (IARC). Agents classified by the IARC monographs, Volumes 1-123 [Internet]. 2018 [cited 2021 Jul 1]. Available from: https://monographs.iarc.who.int/wp-content/uploads/2018/09/ClassificationsAlphaOrder.pdf.

Islam MS, Hoque MF. Concentrations of heavy metals in vegetables around the industrial area of Dhaka city, Bangladesh and health risk assessment. International Food Research Journal 2014;21(6):2121-6.

Jankeaw M, Tongphanpharn N, Khomrat R, Iwai CB, Pakvilai N. Heavy metal contamination in meat and Crustaceans products from Thailand local markets. International Journal of Environmental and Rural Development 2015;6(2):153-8.

Järup L. Hazards of heavy metal contamination. British Medical Bulletin 2003;68(1):167-82.

Kerdthep P, Tongyonk L, Rojanapantip L. Concentrations of cadmium and arsenic in seafood from Muang District, Rayong Province. Journal of Health Research 2009;23(4): 179-84.

Ketsa S, Wisutiamonkul A, Palapol Y, Paull RE. The durian: Botany, horticulture, and utilization. Horticultural Reviews 2020;47:125-211.

Kim NH, Hyun YY, Lee KB, Chang Y, Rhu S, Oh KH, et al. Environmental heavy metal exposure and chronic kidney disease in the general population. Journal of Korean Medical Science 2015;30(3):Article No. 272.

Kinuthia GK, Ngure V, Beti D, Lugalia R, Wangila A, Kamau L. Levels of heavy metals in wastewater and soil samples from open drainage channels in Nairobi, Kenya: Community health implication. Scientific Reports 2020;10(1):1-13.

Kladsomboon S, Jaiyen C, Choprathumma C, Tusai T, Apilux A. Heavy metals contamination in soil, surface water, crops, and resident blood in Uthai District, Phra Nakhon Si Ayutthaya, Thailand. Environmental Geochemistry and Health 2020; 42(2):545-61.

Klinsawathom T, Songsakunrungrueng B, Pattanamahakul P. Heavy metal concentration and risk assessment of soil and rice in and around an open dumpsite in Thailand. EnvironmentAsia 2017;10(2):53-64.

Kumar A, Kumar A, Cabral-Pinto M, Chaturvedi AK, Shabnam AA, Subrahmanyam G, et al. Lead toxicity: Health hazards, influence on food chain, and sustainable remediation approaches. International Journal of Environmental Research and Public Health 2020;17(7):Article No.2179.

Lactusu R, Rauta C, Carstea S, Ghelase I. Soil-plant-man relationships in heavy metal polluted areas in Romania. Applied Geochemistry 1996;11(1-2):105-7.

Li R, Wu H, Ding J, Fu W, Gan L, Li Y. Mercury pollution in vegetables, grains and soils from areas surrounding coal-fired power plants. Scientific Reports 2017;7(1):1-9.

Li Y, Ye F, Wang A, Wang D, Yang B, Zheng Q, et al. Chronic arsenic poisoning probably caused by arsenic-based pesticides: Findings from an investigation study of a household. International Journal of Environmental Research and Public Health 2016;13(1):Article No.133.

Lim LLY, Seubsman SA, Sleigh A. Validity of self-reported weight, height, and body mass index among university students in Thailand: Implications for population studies of obesity in developing countries. Population Health Metrics 2009;7:Article No. 15.

Liščáková P, Nawaz A, Molnárová M. Reciprocal effects of copper and zinc in plants. International Journal of Environmental Science and Technology 2022;19:9297-312.

Lorestani B, Merrikhpour H, Cheraghi M. Assessment of heavy metals concentration in groundwater and their associated health risks near an industrial area. Environmental Health Engineering and Management Journal 2020;7(2):67-77.

Madejón P, Marañón T, Murillo JM. Biomonitoring of trace elements in the leaves and fruits of wild olive and holm oak trees. Science of the Total Environment 2006;355(1-3):187-203.

Mensah E, Kyei-Baffour N, Ofori E, Obeng G. Influence of Human Activities and Land Use on Heavy Metal Concentrations in Irrigated Vegetables in Ghana and their Health Implications. Appropriate Technologies for Environmental Protection in the Developing World: Springer; 2009. p. 9-14.

Ministry of Public Health, Thailand (MoPH). Standard for Contaminants in Food: Volume 137. Bangkok: The Government Gazette; 2020.

Ministry of Agriculture and Cooperatives. Method of Sampling for the Determination of Pesticide Residues. Thai agricultural standard, TAS 9025-2008. Bangkok, Thailand: National Bureau of Agricultural Commodity and Food Standards; 2008.

Mohamed H, Haris PI, Brima EI. Estimated dietary intake of essential elements from four selected staple foods in Najran City, Saudi Arabia. Chemistry Central Journal 2019;13: Article No. 73.

Mohammadi AA, Zarei A, Majidi S, Ghaderpoury A, Hashempour Y, Saghi MH, et al. Carcinogenic and non-carcinogenic health risk assessment of heavy metals in drinking water of Khorramabad, Iran. MethodsX 2019;6: 1642-51.

Nilkarnjanakul W, Watchalayann P, Chotpantarat S. Spatial distribution and health risk assessment of As and Pb contamination in the groundwater of Rayong Province, Thailand. Environmental Research 2022;204:Article No. 111838.

Ogwok P, Bamuwamye M, Apili G, Musalima JH. Health risk posed by lead, copper and iron via consumption of organ meats in Kampala City (Uganda). Journal of Environment Pollution and Human Health 2014;2(3):69-73.

Ojekunle OZ, Rasaki A, Taiwo AM, Adegoke KA, Balogun MA, Ojekunle OO, et al. Health risk assessment of heavy metals in drinking water leaching through improperly managed dumpsite waste in Kurata, Ijoko, Sango area of Ogun State, Nigeria. Groundwater for Sustainable Development 2022; 18:Article No. 100792.

Pamonpol K, Tokhun N. Heavy metal contamination at highland agricultural soil at Dan Sai District, Loei Province, Thailand. Journal of Public Health and Development 2019;17(3):13-22.

Radfard M, Yunesian M, Nabizadeh R, Biglari H, Nazmara S, Hadi M, et al. Drinking water quality and arsenic health risk assessment in Sistan and Baluchestan, Southeastern Province, Iran. Human and Ecological Risk Assessment 2018;24:1-17.

Radwan MA, Salama AK. Market basket survey for some heavy metals in Egyptian fruits and vegetables. Food and Chemical Toxicology 2006;44(8):1273-8.

Rayong Provincial Government Center. Information of Rayong Province [Internet]. 2020 [cited 2021 Jun 23]. Available from: http://www.rayong.doae.go.th/eco%20province%2063.pdf. (in Thai).

Satachon P, Keawmoon S, Rengsungnoen P, Thummajitsakul S, Silprasit K. Source and health risk assessment of some heavy metals in non-certified organic rice farming at Nakhon Nayok Province, Thailand. Applied Environmental Research 2019;41(3):Article No. 8.

Satheannoppakao W, Aekplakorn W, Pradipasen M. Fruit and vegetable consumption and its recommended intake associated with sociodemographic factors: Thailand National Health Examination Survey III. Public Health Nutrition 2009;12(11):2192-8.

Seeda A, Abou El-Nour EZ, Mervat G, Zaghloul S. Interaction of copper, zinc, and their importance in plant physiology: Review, acquisition and transport. Middle East Journal of Applied Sciences 2020;10(3):407-34.

Shabbir Z, Sardar A, Shabbir A, Abbas G, Shamshad S, Khalid S, et al. Copper uptake, essentiality, toxicity, detoxification and risk assessment in soil-plant environment. Chemosphere 2020;259:Article No. 127436.

Simasuwannarong B, Satapanajaru T, Khuntong S, Peng-thamkeerati P. Spatial distribution and risk assessment of As, Cd, Cu, Pb, and Zn in topsoil at Rayong Province, Thailand. Water, Air, and Soil Pollution 2012;223(5):1931-43.

Six L, Smolders E. Future trends in soil cadmium concentration under current cadmium fluxes to European agricultural soils. Science of the Total Environment 2014;485:319-28.

Smolders E, Six L. Revisiting and Updating the Effect of Phosphate Fertilizers to Cadmium Accumulation in European Agricultural Soils. Heverlee, Belgium: Division of Soiland Water Management; 2013.

Song B, Lei M, Chen T, Zheng Y, Xie Y, Li X, et al. Assessing the health risk of heavy metals in vegetables to the general population in Beijing, China. Journal of Environmental Sciences 2009;21(12):1702-9.

Striegel L, Chebib S, Dumler C, Lu Y, Huang D, Rychlik M. Durian fruits discovered as superior folate sources. Frontiers in Nutrition 2018;5:Article No. 114.

Swami SB, Thakor N, Haldankar P, Kalse S. Jackfruit and its many functional components as related to human health: A review. Comprehensive Reviews in Food Science and Food Safety 2012;11(6):565-76.

Taiwo AM, Olowookere ZA, Bada BS, Akinhanmi TF, Oyedepo JA. Contamination and health risk assessments of metals in selected fruits from Abeokuta, Southwestern Nigeria. Journal of Food Composition and Analysis 2022;114:Article No. 104801.

Turull M, Komarova T, Noller B, Fontàs C, Díez S. Evaluation of mercury in a freshwater environment impacted by an organomercury fungicide using diffusive gradient in thin films. Science of the Total Environment 2018;621:1475-84.

USEPA's Integrated Risk Information System (IRIS). IRIS Asessment [Internet]. 2022 [cited 2021 Jul 2]. Available from: https://www.epa.gov/iris.

Wanwimolruk S, Kanchanamayoon O, Boonpangrak S, Prachayasittikul V. Food safety in Thailand 1: It is safe to eat watermelon and durian in Thailand. Environmental Health and Preventive Medicine 2015;20(3):204-15.

Wenzl T, Haedrich J, Schaechtele A, Piotr R, Stroka J, Eppe G, et al. Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Food and Feed. Luxembourg: Publication Office of the European Union; 2016.

World Health Organization (WHO). GEMS/Food Regional Diets: Regional per Capita Consumption of Raw and Semi-Processed Agricultural Commodities: Prepared by the Global Environment Monitoring System/Food Contamination Monitoring and Assessment Programme (GEMS/Food). Geneva, Switzerland: Food Safety Department and World Health Organization; 2003.

World Health Organization (WHO). 10 chemicals of public health concern [Internet]. 2020 [cited 2022 Aug 23]. Available from: https://www.who.int/news-room/photo-story/photo-story-detail/10-chemicals-of-public-health-concern.

Xiao M, Li F, Zhang J, Lin S, Zhuang Z, Wu Z. Investigation and health risk assessment of heavy metals in soils from partial areas of Daye City, China. IOP Conference Series: Earth and Environmental Science 2017;64:Article No. 012066.

Zeng F, Wei W, Li M, Huang R, Yang F, Duan Y. Heavy metal contamination in rice-producing soils of Hunan province, China and potential health risks. International Journal of Environmental Research and Public Health 2015; 12(12):15584-93.