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Research Article
Determination of Organophosphate Pesticides Residues in Fruits, Vegetables and Health Risk Assessment Among Consumers in Chiang Mai Province, Northern Thailand

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Abstract

Background: The group of insecticide which is high effective to prevent and control pest on crop cultivation is organophosphate insecticides (OPs) group. **Methodology:** In this study 17 organophosphate insecticides residues in 126 fruits and 73 vegetable samples were investigated from wet market and supermarkets around Muang district, Chiang Mai province, Northern Thailand. **Results:** The OPs insecticides were determinative by gas chromatography-flame photometric detection (GC-FPD). The most common residue was chlorpyrifos (21.43% in fruit sample and 31.50% in vegetable samples). The residue in sample found not to exceed maximum residue limit (MRL) of Codex Thai and Codex WHO/FAO. Furthermore, the residues of profenofos and triazophos in orange samples were exceeding MRL of Codex WHO/FAO (0.07 mg kg^{-1}) at 0.531 and 0.118 mg kg^{-1}, respectively. The residue concentration data were used for OPs risk assessing from fruits and vegetables intake. The 261 consumers who work in Chiang Mai government center were assed risk from OPs intake by using Hazard Index (HI). The HI was calculated for short and long term risk of toxicity and assess by parameter of risk (<100% indicates that there was no risk of toxic effects and >100% indicates that risk of poisoning). The short-term risk assessed in consumers male, female and overview were shown aHI at 77.08, 62.15 and 56.32%, respectively and long-term risk assessment was shown cHI 109.39, 88.21 and 79.94%, respectively. **Conclusion:** The results shown had no risk of toxicity among this group of consumers except men consumers who had health risk of chronic toxicity.

Key words: Organophosphate residue, GC-FPD, health risk assessment, consumers, hazard index

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

In Thailand, organophosphate (OP) insecticide group is in top 10 lists of agricultural chemicals ranked by insecticides imported in 2014. The most used of OP pesticides include chlorpyrifos, profenophos, dimethoate and ethion[1]. Organophosphate (OP) pesticides are the most commonly used pesticides among Thai farmers for growing fruit and vegetables to markets[2]. With their use, the risk of residues remaining on the food consumed is present and then the governments and international organizations have published a list of pesticides and maximum limits (MRLs) to avoid the health hazard caused by pesticide residues. However, the OP insecticides can be resulted in occurrence of residues of these chemicals and their metabolites in every component of environment i.e., air, water and soil along with that in the crops, vegetables and fruits.

In fresh fruits and vegetables presence amount of nutrients and minerals that important to healthy diet and play an important role in the prevention of chronic diseases. However, vegetable and fruit which sell in market can be source of pesticides which destroy consumer's health. The structure of OPs contains ester structure with decomposing on the surfaces and interiors of fruit and vegetable. Their toxicity of OPs is inhibiting of cholinesterase activity i.e., acethylcholinesterase and butylrylcholinestease especially acetylcholinesterase enzyme which controlling the functions of the nervous system[3,4]. The OPs can be permanently bound the group hydroxylating the enzyme, which prevents acetylcholinesterase from decomposing and gain more amount of acetylcholine at the synapses then leading to a state of hyper arousal, paralysis of the muscles and the main respiratory center. Long-term exposure to pesticides is increasingly suspected of being linked to a broad spectrum of medical problems such as cancer, neurotoxic effects, reproductive health concerns and endocrine disruption, particularly for specific populations[5-8].

The most route of OPs exposure through consumption of fruits and vegetable continue every day[9-12] so that the food monitoring and health risk assessment from OPs exposure would be necessary in order to protect consumer health, improve the management of agricultural resources and prevent economic losses[13]. The assessment of exposure with residues of OP pesticides in the fruits and vegetables were related human health risk assessment. Risk assessment typically further divided into similar, but separate practices, depending on whether the chemical being evaluated carcinogen or non-carcinogen. The major difference in the calculations of carcinogenic and non-carcinogenic risks involves the method by which risks from low level exposures are determined[14,15].

The workers who work in Chiang Mai government center are consumers who from every parts of Chiang Mai province. They consume fruit and vegetable from market around Chiang Mai city so they can be exposed OPs from residue fruit and vegetable. The aim of this study was to analyze organophosphates insecticide residues in fruits and vegetables and to assess insecticide dietary intake in population of Chiang Mai province. That OP pesticides residue in fruits and vegetables will be harmful to consumers or has accumulated in the long term.

MATERIALS AND METHODS

Reagents and chemicals: Certified individual pesticide standards, namely azinphos-ethyl (99.0%), azinphos-methyl (99.0%), chlorpyrifos (98.0%), diazinon (99.0%), dicrotophos (99.0%), dimethoate (98.5%), EPN (99.0%), ethion (98.0%), fenitrothion (98.0%), malathion (99.0%), methamidophos (98.5%), methidathion (98.0%), mevinphos (99.0%), monocrotophos (98.5%), parathion-methyl (98.5%), pirimiphos-methyl (99.0%), prothiofos (94%), profenofos (98.5%) and trizophos (80%) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Individual stock standard solutions (1000 mg L^{-1}) were prepared by dissolving an accurate weight of each pesticide in 100 mL of ethyl acetate. Working standards solutions (10 mg L^{-1}) for the 19 OPs were prepared by serial dilution of individual stock with ethyl acetate. All standard were stored under refrigeration at -20°C. Ethyl acetate Actual analysis (J.T. Baker, USA) were HPLC (analysis grade) (>99%) and sodium chloride (>99.5%) was obtained from Merck (Darmstadt, Germany).

Study site, sampling and preparation of sample: The fruit and vegetable samples were collected on August-September, 2015 from wet market and supermarket around Muang District of Chiang Mai province. Eight kinds of fruit (orange, apple, pear, dragon fruit, strawberry, guava, green and red grape) and 6 kinds of vegetable (kale, yard long bean, spring onion, coriander, morning glory and cucumber) were collected for OPs analyzing.

One kilogram of each sample was collected and shaped to small piece and stepwise sampling was performed until the final sample weighed 300 g was randomly taken for analysis. All samples were stored at -20°C throughout the experimental period. The OP compounds analyzed in fruit

samples included methamidophos, mevinphos, dimethoate, diazinon, parathion-methyl, pirimiphos-methyl, fenitrothion, malathion, chlorpyrifos, methidathion, prothiophos, profenofos, ethion, triazophos, EPN and azinphos-methyl and azinphos-ethyl.

Sample extraction and conditions of gas chromatography-flame photometric detector: Sample extraction and analysis were modified from the method of Fillion *et al.*[16]. Briefly, 5 g of fruit samples was weighed into a 50 mL centrifuge tube followed by the addition of 24 mL acetonitrile (HPLC grade; JT Baker, USA). Fifty microliter of 4 μg mL^{-1} triphenylphosphate (internal standard [IS]) was added and subsequently shaker by vortex mix for 5 min. The supernatant was transferred to a 50 mL centrifuge tube with addition of 3 g of NaCl and add 3 mL of 0.5 M phosphate buffer, pH 7.0 then centrifuged again at 20×1000 rpm for 3 min. Used dropper to filter papers No. 1 (Whatman, Piscataway, USA) to contain Na_2SO_4 3 g to bottle evaporation. Add 6 mL acetonitrile extract and washing by 2 mL ethyl acetate. Then dry evaporation by ratory vacuum 37°C, then washing by 5 mL ethyl acetate then dropper 2 mL past PSA mix and centrifuge at 13,000 rpm for 3 min the extract was evaporated with a gentle stream of nitrogen at room temperature and subsequently reconstituted in 200 mL of ethyl acetate for Gas Chromatography (GC) analysis.

The GC analysis consisted of a Hewlett-Packard model 6890 equipped with a flame photometric detector, a capillary column (DB-5MS, 0.25 mm 9, I.D. 9, 30 m length 9, 0.25 1 m film thickness (J and W column; Agilent Technologies, USA) and a computerized data handling system (GC Chemstation A.10.02; Agilent Technologies, USA). Temperature was 220°C for the injection port (splitless mode). Temperature programming of the oven was as follows: Initial temperature of 100°C for 10 min, first ramp at 15°C min^{-1} to 180°C for 5 min, second ramp at 5°C min^{-1} to 250°C for 3 min and final temperature maintained at 290°C for 4 min. The carrier gas was helium 99.999%. Chromatograms of OP compounds were shown in Fig. 1.

Health risk assessment: The OPs pesticides exposure from fruit and vegetable consumption Chiang Mai province, Thailand were assessed. The data from 24 h food recalled questionnaires were used for estimating OPs intake. The data from participants who consumed fruit and vegetable were selected and calculated to fruit and vegetable consume per day by NutriFact program[17,18].

The assessment of exposure to acute/short-term consumer health risk (aHI) on the Estimated Short Term Intake (ESTI) was calculated according to report from Liu *et al.*[19]. The dietary exposure to OPs pesticides was calculated based on acute reference dose (ARfD) and chronic/long-term consumer health risk (hazard quotient, HQ) was calculated based on the Estimated Daily Intake (EDI) and the Acceptable Daily Intake (ADI). For the precise evaluation, the ARfD and ADI are expressed as a percentage of daily intakes for a mean kilogram per person. The Hazard Quotient (HQ) indicates an unacceptable risk when it is higher than 100% and the higher aHI/HQ value represents the higher risk.

The cumulative risk index (cHI) will be used for the sum of HQs from the multiple pesticide residues that the consumer is exposed to, which is calculated by summing the hazard quotients (HQs) for each pesticide in the samples.

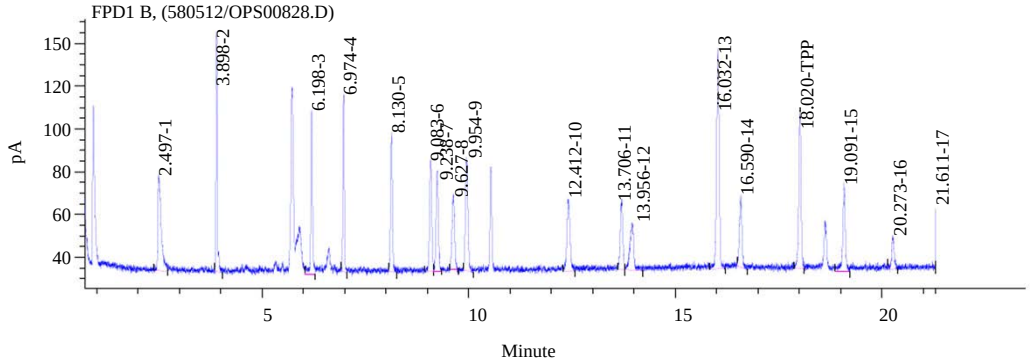

Fig. 1: Chromatogram of standard OPs from gas chromatography-flame photometry detection (GC-FID). The OP standard compounds at concentration of 100 μg mL^{-1}. 1: Methamidophos, 2: Mevinphos, 3: Dimethoat, 4: Diazinon, 5: Parathion-methyl, 6: Pirimiphos-methyl, 7: Fenithothion, 8: Malathion, 9: Chlorpyrifos, 10: Methidathion, 11: Prothiophos, 12: Profenofos, 13: Ethion, 14: Triazophos, 15: EPN, 16: Azinphos-methyl and 17: Azinphos-ethyl

RESULTS AND DISCUSSION

Quality control: The chromatogram of standard OPs were shown good separation (Fig. 1). The quality controls parameters were listed in Table 1. Limit of detection (LOD) and limit of quantification (LOQ) for all of OPs ranged from 0.002-0.003 and 0.004-0.005 mg kg^{-1}, respectively. The recoveries of the compounds ranged from 83.63-117.70% for low spiked level, 85.70-111.18% for medium spiked level and 94.27-114.40% for high spiked level. Relative SD coefficient (%RSD) of intra-batch ranged from 1.47-18.14% for low spiked level, 0.79-7.88% for medium level and 0.05-12.80% for high spiked level. Percentage of RSD inter-batch ranged from 1.74-8.55%.

OPs residues in fruits and vegetables: The modified method gave good precision and could be used for analyzing OPs in samples. The 17 OPs were analyzed in fruit and vegetables; the result of residue was shown in Table 2. The OPs residues in fruit and vegetable samples are listed in Table 2. The OPs detected in fruit samples through 17 pesticides in 126 fruits samples had 8 kind (orange, apple, pear, dragon fruit, strawberry, guava, green grape and red grape) and 73 vegetable samples had 7 kinds (kale, false pakchoi, yard long bean, spring onion, coriander, morning glory and cucumber) from market around Chiang Mai province, Northern Thailand. Pesticide was determinate by gas chromatography-flame photometric detected (GC-FPD).

The chlorpyrifos was detected in all kind of fruit and vegetable samples. The OP pesticides detected in fruit samples from 5 supermarket 74 sample included orange, apple, pear, dragon fruit, strawberry, guava, green and red grape. The common OP pesticides detected in supermarket samples were chlorpyrifos (26.31%), methidathion (20.27%) and ethion (11.84%), respectively. The OPs detected in wet market sample were ethion (20.83%), chlorpyrifos (14.58%) and diazinon and malathion (8.33%), respectively. The most common residue in fruit sample was chlorpyrifos (21.43%). In addition, there were some residue in the samples i.e., methamidophos, dimethoate, fenitrothion, diazinon, malathion, methidathion, prothiophos, profenofos, ethion and triazophos.

The chlorpyrifos is the most detected in fruit and vegetable samples, this situation play like the of previous studies[20]. In comparison of OPs detection in fruit samples among wet market and supermarkets around Muang district, Chiang Mai province found the number of residue in supermarket higher than wet market. Among the detected compounds, chlorpyrifos and ethion were most detected from all sources. The highest level in fruit sample was found in orange and pear (ethion 0.796 and 0.877 mg kg^{-1}). The sample found not to exceed Maximum Residue Limit (MRL) of Codex Thai and Codex WHO/FAO[21]. Furthermore, the residues of profenofos and triazophos in orange samples were exceeding MRL of Codex WHO/FAO[21] (0.07 mg kg^{-1}) at 0.463-0.600 and 0.193 mg kg^{-1}, respectively of supermarket samples. The sample found not to exceed Maximum Residue Limit (MRL) of Codex Thai[22] and Codex WHO/FAO and EU. Furthermore, the residues of profenofos and triazophos in orange samples were exceed MRL of Codex WHO/FAO (0.07 mg kg^{-1}) at 0.531 and 0.118 mg kg^{-1}, respectively and dimethoate, diazinon, profenofos, ethion, triazophos

Table 1: Quality control parameters of OPs analyzing by using GC-FPD

					Recovery percentage of SD (n = 3)			Interbatch percentage of RSD (n = 3)			
OP compound	Retention time (min)	R	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	Low	Medium	High	Low	Midium	High	Interbatch RSD% (n = 5)
Methamidophos	2.519	0.9961	0.003	0.005	92.43 (±2.45)	89.88 (±6.84)	99.74 (±1.30)	10.62	7.61	0.33	6.79
Mevinphos	3.910	0.9972	0.002	0.005	83.63 (±4.71)	97.40 (±7.05)	104.68 (±10.23)	18.14	6.88	2.41	8.55
Dimethoate	6.224	0.9969	0.002	0.005	86.93 (±1.19)	85.70 (±0.69)	99.41 (±9.06)	5.46	0.80	2.28	1.74
Diazinon	6.991	0.9977	0.002	0.005	99.73 (±0.37)	96.89 (±4.58)	98.03 (±13.44)	1.47	4.72	3.43	6.71
Parathion-methyl	8.159	0.9992	0.002	0.005	94.00 (±2.00)	95.19 (±5.12)	99.83 (±5.64)	8.52	5.38	1.41	5.58
Pirimiphos-methyl	9.100	0.9995	0.002	0.005	99.15 (±1.47)	92.08 (±1.45)	99.02 (±8.95)	5.93	1.58	2.26	4.95
Fenitrothion	9.256	0.9987	0.002	0.005	95.96 (±1.64)	93.25 (±3.68)	97.94 (±8.34)	6.84	3.94	2.13	3.33
Malathion	9.608	0.9981	0.002	0.005	94.55 (±0.90)	98.15 (±2.43)	98.90 (±2.64)	3.81	2.47	0.67	3.80
Chlorpyrifos	9.978	0.9963	0.002	0.005	114.61 (±11.05)	111.18 (±11.50)	114.32 (±62.99)	17.44	7.88	12.80	6.67
Methidathion	12.439	0.9976	0.002	0.005	94.47 (±1.11)	87.85 (±6.23)	98.77 (±14.09)	4.70	7.10	3.57	5.43
Prothiophos	13.720	0.9987	0.002	0.005	94.04 (±0.72)	94.74 (±0.75)	96.72 (±3.11)	3.06	0.79	0.80	5.87
Profenofos	13.980	0.9989	0.002	0.005	93.04 (±1.66)	87.07 (±2.13)	97.54 (±16.05)	7.14	2.45	4.11	2.47
Ethion	16.058	0.9978	0.002	0.004	117.70 (±1.22)	92.95 (±2.76)	98.36 (±0.20)	5.19	2.97	0.05	4.88
Triazophos	16.628	0.9990	0.002	0.005	95.85 (±1.03)	88.73 (±4.79)	98.37 (±1.58)	4.29	5.40	0.40	3.83
EPN	19.109	0.9979	0.002	0.005	97.93 (±0.94)	98.28 (±1.63)	98.37 (±3.81)	3.85	1.66	0.97	5.50
Azinphos-methyl	20.337	0.9962	0.003	0.005	89.95 (±1.04)	91.95 (±2.80)	94.27 (±21.52)	4.62	3.04	5.71	6.67
Azinphos-ethyl	21.631	0.9988	0.002	0.005	93.64 (±1.07)	97.79 (±3.26)	95.94 (±6.85)	4.55	3.33	1.79	6.50

RSD%: (SD/mean) × 100

Table 2: OPs residues in fruit and vegetable samples from market and supermarket in around Chiang Mai district of Chiang Mai province

Fruits	No. of samples detected	Name of OP residue detected	No. of residues samples (%)	Concentration of OP residues detected (mg kg^{-1})	MRL (mg kg^{-1})		
					CODEX[a]	EU	Thailand
Fruit samples (n = 124)							
Orange	14	Dimethoate	1 (7.14)	0.042	5	0.02	5
		Diazinon	3 (21.43)	0.027±0.020	NR	0.01	NR
		Malathion	5 (35.71)	0.221±0.137	7	2	7
		Chlorpyrifos	11 (78.57)	0.082±0.128	1	0.3	1
		Prothiophos	1 (7.14)	0.002	NR	NR	NR
		Profenofos	2 (14.29)	0.531±0.097	NR	0.01	NR
		Ethion	11 (78.57)	0.294±0.295	NR	0.01	NR
		Triazophos	11 (78.57)	0.118±0.104	NR	0.01	NR
Apple	11	Diazinon	3 (27.27)	0.001±0.000	0.3	0.01	0.3
		Chlorpyrifos	1 (9.09)	0.003	1	0.01	1
		Ethion	1 (9.09)	0.001	NR	0.01	NR
Pear	10	Diazinon	1 (10)	0.001	NR	0.01	0.3
		Malathion	1 (10)	0.059	NR	0.02	NR
		Methidathion	4 (40)	0.027±0.024	1	0.03	1
		Ethion	1 (10)	0.877	NR	0.01	NR
Dragon fruit	11	Methidathion	2 (20)	0.004±0.003	NR	NR	NR
Strawberry	10	Chlorpyrifos	1 (10)	0.03	0.3	0.2	NR
Guava	30	Malathion	2 (6.66)	0.002±0.002	NR	0.02	NR
		Chlorpyrifos	11 (36.66)	0.017±0.015	NR	0.05	NR
		Methidathion	11 (36.66)	0.009±0.004	NR	0.02	NR
		Prothiophos	1 (3.33)	0.004	NR	NR	NR
		Profenofos	1 (3.33)	0.006	NR	0.01	NR
		Ethion	6 (20)	0.015±0.009	NR	0.01	NR
		Triazophos	1 (3.33)	0.002	NR	0.01	NR
Green grape	12	Chlorpyrifos	1 (8.33)	0.002	0.5	0.3	0.5
Red grape	24	Fenitrothion	1 (4.16)	0.002	NR	0.01	NR
		Chlorpyrifos	2 (8.33)	0.015±0.012	0.5	0.3	0.5
		Methidathion	1 (4.16)	0.088	1	0.02	1
Vegetable samples (n = 73)							
Kale	8	Chlorpyrifos	1 (12.5)	0.22	NR	0.05	NR
Yard long bean	8	Chlorpyrifos	2 (25)	0.006±0.005	NR	NR	0.05
		Profenofos	2 (25)	0.003±0.000	NR	NR	0.01
Spring onion	9	Chlorpyrifos	2 (22.22)	0.005±0.000	0.2	0.05	NR
		Ethion	1 (11.11)	0.0002	NR	0.02	NR
Coriander	12	Chlorpyrifos	9 (75)	0.019±0.022	NR	5	0.05
		Profenofos	1 (8.33)	0.003	NR	0.05	0.05
Morning glory	15	Chlorpyrifos	2 (13.33)	0.041±0.045	NR	NR	0.05
Cucumber	14	Chlorpyrifos	6 (42.85)	0.024±0.019	NR	0.05	NR

NR: No report of estalished MRLs, [a]Determined by CODEX Alimentarius Commission, [b]Determined by European Commission regulation No. 1107/2009, (update 07 July, 2015)

in orange samples were exceed MRL of EU[23] at 0.042>0.02, 0.027>0.01, 0.531>0.01, 0.294>0.01 and 0.118>0.01 m g kg^{-1}, respectively, malathion and ethion in pear samples were exceed EU-MRL[23] at 0.059>0.01 and 0.877>0.01 mg kg^{-1}, respectively. The detected concentration of methidathion in red grape and chlorpyrifos in kale samples were exceed EU-MRL at 0.088 and 0.22 mg kg^{-1}, respectively.

Health risk assessments in consumers who consumed OPs contaminated fruit and vegetable: The most volunteer's consumers had age between 21-60 years old. They have been working in government office at Chiang Mai province 8 h day^{-1} (80% times working in their office). Mean body weights of male, female and whole group were 68.93, 57.07 and 60.36, respectively consumptions. The mean of male consumed fruit and vegetable were 76.22 and 23.04 g day^{-1} while female were 64.68 and 29.66 g day^{-1}.

Acute and chronic cumulative intakes of OPs residue were calculated. The Hazard Index (HI) was used as parameter of risk (<100% indicates that there was no risk of toxic effects and >100% indicates that risk of poisoning). The risks of short-term and long-term were calculated. The short-term risk assessed in consumers male, female and overview were shown aHI at 77.08, 62.15 and 56.32%, respectively and long-term risk assessment was shown cHI 109.39, 88.21 and 79.94%, respectively (Table 3). The result shown had no risk of toxicity among this group of subjects but in long term male

Table 3: Risk estimates based on fruit and vegetable comparison of consumed OPs residue in the highest concentration with acute reference doses

			ESTI			aHI = ESTI/ARfD×100			EDI			HQ = EDI/ADI×100		
Residue in fruit samples	ADI std	ARfD std	Man (n = 16)	Women (n = 46)	Total (n = 62)	Man (n = 16)	Women (n = 46)	Total (n = 62)	Man (n = 16)	Women (n = 46)	Total (n = 62)	Man (n = 16)	Women (n = 46)	Total (n = 62)
Methamidophos	0.004	0.01	0.000002	0.000002	0.000002	0.0212963	0.02024546	0.02032882	0.000002	0.000002	0.000002	0.053	0.051	0.051
Dimethoate	0.002	0.02	0.000089	0.000085	0.000085	0.44722222	0.42515475	0.42690529	0.000089	0.000085	0.000085	4.472	4.252	4.269
Diazinon	0.001	0.03	0.000085	0.000081	0.000081	0.28395062	0.26993952	0.27105098	0.000026	0.000024	0.000024	2.556	2.429	2.439
Fenitrothion	0.006	0.04	0.000004	0.000004	0.000004	0.01064815	0.01012273	0.01016441	0.000043	0.000040	0.000041	0.710	0.675	0.678
Malathion	0.3	2	0.000788	0.000749	0.000752	0.03939815	0.03745411	0.03760832	0.000313	0.000298	0.000299	0.104	0.099	0.100
Chlorpyrifos	0.003	0.1	0.000931	0.000885	0.000888	0.93064815	0.88472679	0.88836958	0.000092	0.000087	0.000087	3.052	2.902	2.914
Methidathion	0.001	0.01	0.000187	0.000178	0.000179	1.87407407	1.78160085	1.78893646	0.000032	0.000030	0.000030	3.194	3.037	3.049
Prothiophos	1E-04	-	0.000009	0.000008	0.000008	-	-	-	0.000006	0.000006	0.000006	6.389	6.074	6.099
Profenofos	0.03	1	0.001278	0.001215	0.001220	0.12777778	0.12147279	0.12197294	0.000760	0.000723	0.000726	2.534	2.409	2.419
Ethion	0.002	-	0.001868	0.001776	0.001783	-	-	-	0.000471	0.000447	0.000449	23.532	22.371	22.463
Triazophos	0.001	0.001	0.000411	0.000391	0.000392	41.1018519	39.073746	39.2346292	0.000170	0.000162	0.000163	17.037	16.196	16.263
											CHI	63.630	60.490	60.740
Residue in vegetable samples			(n = 36)	(n = 94)	(n = 130)	(n = 36)	(n = 94)	(n = 130)	(n = 36)	(n = 94)	(n = 130)	(n = 36)	(n = 94)	(n = 130)
Diazinon	0.001	0.03	0.0000004	0.0000006	0.0000004	0.0012235	0.0019049	0.0014275	0.0000004	0.0000006	0.0000004	0.037	0.057	0.043
Chlorpyrifos	0.003	0.1	0.0000734	0.0001143	0.0000857	0.0734412	0.1143487	0.0856917	0.0000093	0.0000145	0.0000109	0.310	0.483	0.362
Profenofos	0.03	1	0.0000013	0.0000020	0.0000015	0.0001268	0.0001974	0.0001479	0.0000011	0.0000017	0.0000013	0.004	0.006	0.004
Ethion	0.002	-	0.0000001	0.0000001	0.0000001	-	-	-	0.0000001	0.0000001	0.0000001	0.003	0.005	0.004
											CHI	0.350	0.550	0.413

consumers had risk of toxicity but not in female consumers. The cumulative risk (cHI) for the OPs in present study was higher than other study that mean the group of consumers in Chiang Mai province more consumed residues fruit and vegetable or environmental exposure than other studies[19,24].

CONCLUSION

The most analyzed of 126 fruits and 73 vegetables were detected chlorpyrifos. The sample found not to exceed Maximum Residue Limit (MRL) of Codex Thai and Codex WHO/FAO. Furthermore, the residues of Profenofos and Triazophos in orange samples were exceeding MRL of Codex WHO/FAO (0.07 mg kg^{-1}) at 0.531 and 0.118 mg kg^{-1}, respectively. The OPs i.e., dimethoate, diazinon, profenofos, ethion and triazophos in orange samples, malathion, ethion in pear samples, methidathion in red grape samples and chlorpyrifos in kale samples were exceed of MRL of EU[23]. The risk of exposure from intake residues fruit and vegetable were assessed assessment. The Hazard Index (HI) among consumers in Chiang Mai province were no risk of toxicity except the male consumers had long term or chronic risk of toxicity.

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REFERENCES

1. DOA., 2015. Statistic data: Acts of hazardous materials. Department of Agriculture, Ministry of Agriculture and Cooperatives, Bangkok, Thailand. http://www.doa.go.th/main/, (In Thai)
2. Hongsibsong, S., T. Kerdnoi, W. Polyiem, V. Patarasiriwong and T. Prapamontol, 2015. Organophosphate pesticide exposure of farmers in Chiang Mai province, Northern Thailand. Proceedings of the International Conference on International Conference on Advances in Environment Research, July 29-30, 2015, Jeju Island, South Korea, pp: 73-76.
3. Neupane, D., E. Jors and L. Brandt, 2014. Pesticide use, erythrocyte acetylcholinesterase level and self-reported acute intoxication symptoms among vegetable farmers in Nepal: A cross-sectional study. Environ. Health, Vol. 13. 10.1186/1476-069X-13-98.
4. Pathak, M.K., M. Fareed, A.K. Srivastava, B.S. Pangtey, V. Bihari, M. Kuddus and C. Kesavachandran, 2013. Seasonal variations in cholinesterase activity, nerve conduction velocity and lung function among sprayers exposed to mixture of pesticides. Environ. Sci. Pollut. Res., 20: 7296-7300.
5. Mostafalou, S. and M. Abdollahi, 2013. Pesticides and human chronic diseases: Evidences, mechanisms and perspectives. Toxicol. Applied Pharmacol., 268: 157-177.
6. Freeman, L.E.B., M.R. Bonner, A. Blair, J.A. Hoppin and D.P. Sandler *et al*., 2005. Cancer incidence among male pesticide applicators in the agricultural health study cohort exposed to diazinon. Am. J. Epidemiol., 162: 1070-1079.
7. Paz-y-Mino, C., G. Bustamante, M.E. Sanchez and P.E. Leone, 2002. Cytogenetic monitoring in a population occupationally exposed to pesticides in Ecuador. Environ. Health Perspect., 110: 1077-1080.
8. George, J. and Y. Shukla, 2011. Pesticides and cancer: Insights into toxicoproteomic-based findings. J. Proteomics, 74: 2713-2722.
9. Bencivenga, B., G. Pasquazi, M. Bonifazi, S. DeVincenzi, I. Rosatelli and T. Simonetti, 1997. Pesticide-residues survey on fruit and vegetable products on the market of Rome and of the Lazio region. Industrie Alimentari, 36: 1005-1008.
10. Dorea, H.S., J.L. Tadeo and C. Sanchez-Brunete, 1996. Determination of organophosphorus pesticide residues in fruits by gas chromatography with ITD and NPD detection. Chromatographia, 43: 380-386.
11. Wolejko, E., B. Lozowicka and P. Kaczynski, 2014. Pesticide residues in berries fruits and juices and the potential risk for consumers. Desalination Water Treat., 52: 3804-3818.
12. Syed, J.H., A. Alamdar, A. Mohammad, K. Ahad and Z. Shabir *et al*., 2014. Pesticide residues in fruits and vegetables from Pakistan: A review of the occurrence and associated human health risks. Environ. Sci. Pollut. Res., 21: 13367-13393.
13. Gray, G. M. and J.K. Hammitt, 2000. Risk/risk trade-offs in pesticide regulation: An exploratory analysis of the public health effects of a ban on organophosphate and carbamate pesticides. Risk Anal., 20: 665-680.
14. Lu, C., F.J. Schenck, M.A. Pearson and J.W. Wong, 2010. Assessing children's dietary pesticide exposure: Direct measurement of pesticide residues in 24-hr duplicate food samples. Environ. Health Perspect., 118: 1625-1630.
15. Albertini, R., M. Bird, N. Doerrer, L . Needham, S. Robison, L. Sheldon and H. Zenick, 2006. The use of biomonitoring data in exposure and human health risk assessments. Environ. Health Perspect., 114: 1755-1762.
16. Fillion, J., F. Sauve and J. Selwyn, 2000. Multiresidue method for the determination of residues of 251 pesticides in fruits and vegetables by gas chromatography/mass spectrometry and liquid chromatography with fluorescence detection. J. AOAC Int., 83: 698-713.

17. Chuayen, J., K. Rerkasem, J. Wungrath, R. Khampan and N. Pinmas *et al*., 2015. Development of NutriFact program for the nutritive values of Thai and local Northern Thai recipes. Proceedings of the 9th Thailand Congress of Nutrition, October 21-23, 2015, Siam Paragon, Bangkok.
18. Rerkasem, K., R. Khampan, J. Chuayen and J. Wungrath, 2015. Nutritional values of local northern Thai style chili paste with NutriFact program. Proceedings of the 9th Thailand Congress of Nutrition, October 21-23, 2015, Siam Paragon, Bangkok.
19. Liu, Y., D. Shen, S. Li, Z. Ni, M. Ding, C. Ye and F. Tang, 2016. Residue levels and risk assessment of pesticides in nuts of China. Chemosphere, 144: 645-651.
20. Sapbamrer, R. and S. Hongsibsong, 2014. Organophosphorus pesticide residues in vegetables from farms, markets and a supermarket around Kwan Phayao lake of Northern Thailand. Arch. Environ. Contam. Toxicol., 67: 60-67.
21. WHO/FAO., 2012. Further guidance on derivation of the acute RfD. In: Pesticide Residues in Food-2002, WHO/FAO, Rome, Italy, pp: 4-8.
22. Central Lab Thai, 2015. Importing country Maximum Residue Limits (MRLs). Central Laboratory (Thailand) Co. Ltd., Chatuchak, Bangkok, Thailand. http://www. centrallabthai. com/, (In Thai)
23. EU., 2015. European Commission food, plant pesticides residue database.http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=homepage&lang uage=EN
24. Sanchez, Y.A., K. Deener, E.C. Hubal, C. Knowlton, D. Reif and D. Segal, 2010. Research needs for community-based risk assessment: Findings from a multi-disciplinary workshop. J. Exposure Sci. Environ. Epidemiol., 20: 186-195.