



Health Risk Assessment of Pesticide Residues in Vegetables from River Basin Area

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Abstract

Environmental contaminations with pesticides are considered as one of the major environmental pathways of human exposure leading to a potential threat to human health, especially if there is an accumulation in the trophic levels. This study purposed to investigate the level of pesticide residues and the potential health risk associated with vegetables, surface water, and sediment obtained from the river basin area. The concentrations of 87 pesticides from four main groups namely; organophosphate, organochlorine, pyrethroid, and persistent organic pollutants (POPs) were verified by triple quadrupole GC-MS/MS. The concentration of Parathion methyl, Methidathion, Bromophos methyl, Chlorfenvinphos, Triazophos, Azinphos ethyl, and D-trans-Phenothrin in the sediment samples ranged from 12.99-19.95 $\mu\text{g kg}^{-1}$. The surface water sample mainly contains p, p'-DDT $<0.012 \mu\text{g L}^{-1}$ followed by Endrin and Dieldrin $<0.08 \mu\text{g L}^{-1}$, and Aldrin, Alpha-BHC, Heptachlor $<0.004 \mu\text{g L}^{-1}$, respectively. The PTI was detected at 0.4 in the sum of surface water samples. The detectable pesticide residues were found in 95% of 20 vegetable samples. The positive of screening vegetables were most obviously contaminated with organophosphate (95%) followed by pyrethroid (40%), organochlorine (20%) and POPs (5%), respectively. The highest concentration of 0.04 mg kg^{-1} was recorded for Dicrotophos in Kitchen mint (*Mentha cordifolia* Opiz ex Fresen). Fenpropathrin recorded the lowest concentration of $3.2 \times 10^{-3} \text{ mg kg}^{-1}$ in corn (*Zea mays* L.). The highest PTI (31.20) was found in corn. The combined risk index of pesticide residues showed significant health risk to humans more than individual risk index. The health risk indices show that the detected pesticides considered a serious public health problem in the studied area, and there is a need to increment their monitoring to reduce their misuse.

Keywords: Health risk; Toxicity screening; Pesticide toxic index; Hazard index; Risk assessment

Introduction

Pesticides were introduced to the field to increase yield in agricultural landscapes and shield crops from insects [1]. As a result, various pesticide residues are often detected in agricultural products. The exploitation of pesticides has enlarged, however cultivated area does not increase, but stays roughly the same. This means that the use of pesticides per area has increased. Yet, pesticides used have become an important part of crop production. The sophisticated amount in pesticides was used to protect crops due to the adaptation and acclimatization of insects resulting in pesticide resistance of insects, as a result, higher pesticide concentration was used and new pesticides were developed [2–3]. They have also been many environmental concerns associated with the widespread pesticide utilization on cultivated areas, such as air, water, soil, sediments, and biological tissues because of low biodegradability and persistence in the environment [1, 4–5]. Consequently, people's awareness has been increased, and the overall quality has become a global concern. Furthermore, the increase in the use of pesticides has resulted in environmental contamination and also caused effects on human health [5].

Many pesticides that are dangerous to humans and the environment are increasingly used to protect crops and to ensure high vegetable production yield [6–7]. Besides, multiple applications of pesticides in the same growing season were used with different combinations of insecticides and fungicide [8]. The harmful effects of pesticide use on human health have become evident. The pesticide use can come into the human body by direct contact with chemicals, through food especially fruits and vegetables, contaminated water or polluted air [9]. Pesticides are known to be a public health issue and have been reported to cause toxic effects on human, ranging from acute effects such as dizziness, headaches, rashes, and nausea

to chronic effects such as cancer, neurotoxicity, genotoxicity, reproductive disorders, and endocrine system dysfunctions [10–13]. Both acute and chronic diseases can result from their exposure. The risks were usually related to toxicity and quantity of the pesticide used, the approach of accomplishment, amount and frequency of contact with pesticide and the person that is exposed during application [14]. Continued exposure to sub-lethal quantities of pesticides for a persistent period (years to decades), results in chronic illness in humans. Incidences of chronic diseases have started to grow as a pesticide has become an increasing part of our ecosystem [15].

The World Health Organization (WHO) [16] reported death globally from pesticide toxicity of about 849,000 people in 2001. Unfortunately, most of pesticide poisoning and death occurred in developing countries [17]. Thailand statistics of morbidity from pesticide poisoning during the years 2001–2017, there were reports of 34,221 pesticide poisoning cases, 49 deaths and an average of 2,013 illnesses per year. The report showed that in 2018, the pesticide poisoning in Thailand that causes the highest morbidity rate in 3 provinces. Roi-Et Province had the highest incidence (37.08), followed by Lampang Province (28.93) and Uttaradit Province (28.44), respectively [18]. Nevertheless, there are few studies on pesticide residues that content in environments in Thailand. Therefore, this study aimed to evaluate the presence of pesticide residues in vegetables, surface water, and sediment obtained from the river basin area. To check the acquiescence of these products with the maximum residue levels (MRLs) requirements set in the international food standards Codex and legal EU regulation, the guidelines of practice contribute to the safety, quality, and fairness of international food trade and to determine the health risk assessment with the exposure as models in toxicity screening for food safety, food quality and sustainable agriculture.

Materials and methods

1) Study area

The researcher survey was undertaken among the Wang River, Lampang Province, the northern of Thailand, as shown in Figure 1. The Wang River is one of the main tributaries of the Chao Phraya River which is the most essential water resource of Thailand. The Wang River lies in the north-south direction, located between latitudes $16^{\circ} 05' N$ and $19^{\circ} 30' N$, and longitudes $98^{\circ} 54' E$ and $99^{\circ} 58' E$. The total catchment area covers about $10,791 \text{ km}^2$. The total length of the Wang River is approximately

460 km [19]. The part of the river is comprised of a vast agriculture area including rice fields, corn, pineapple, and vegetable plantations. Pesticides are used extensively in crop production. The Wang River which receives the runoff from the drainage basin has been impacted by a pesticide used in agriculture production. Each year, during the wet season there is a huge amount of fresh water flowing out to Wang River. Suspended solids, together with organic particles containing pesticides, are transported by runoff to the river [20].

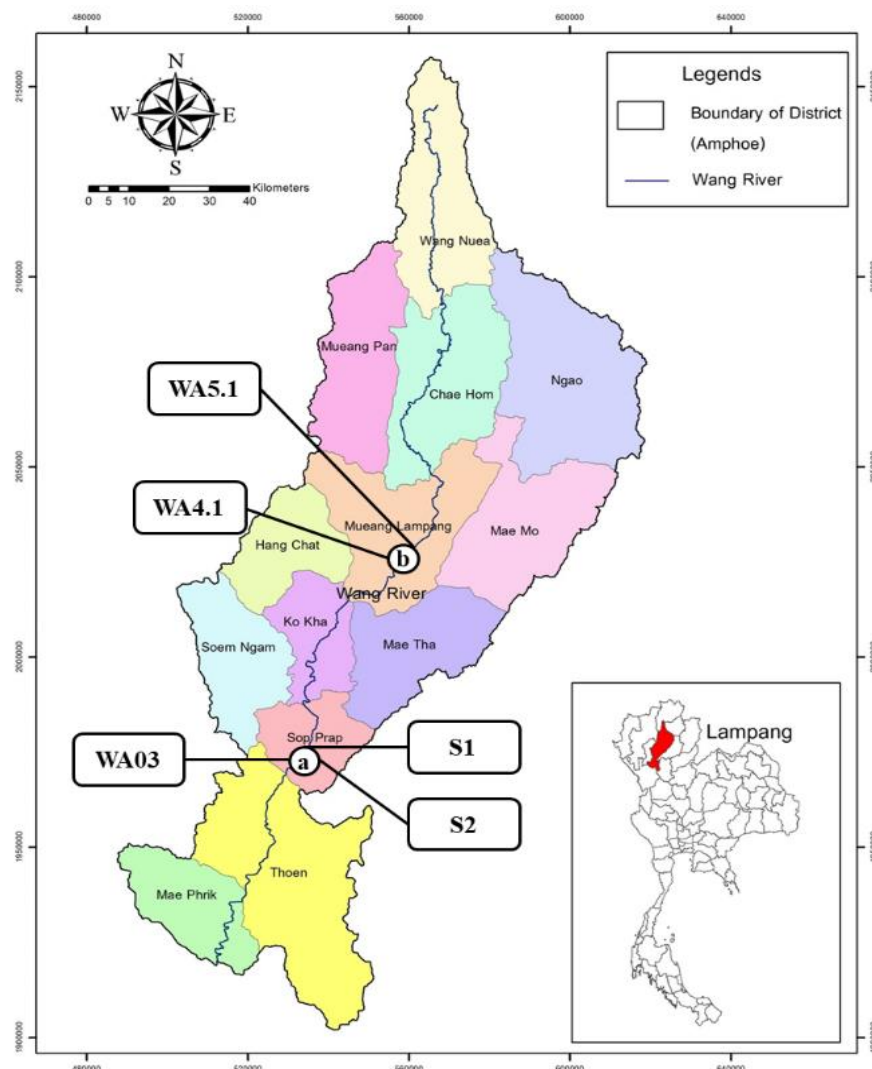


Figure 1 Map of sampling site: (a) sampling site in Sop Prap District, location of farm areas beside Wang River; (S1) sediment sampling location Sop Prap; (S2) sediment sampling location Sop Prap; (WA03) water sampling location Sop Prap pumping stations (b) sampling site in Mueang Lampang District, location of the fresh market; (WA4.1) water sampling location Yang Dam; (WA5.1) water sampling location Pichai Bridge.

2) Quantification of pesticide residues and toxicity screening

2.1) Surface water sample

The pesticide-contaminated of surface water obtained from the files of the Pollution Control Department (PCD) over the period covering wet season (September–November 2018) and dry season (March–May 2019). The water quality parameter measured duplication per dry and wet seasons by the federal.

2.2) Sediment sample

The sediment samples from each sampling site were collected at 0–30 cm depth using a composited. The samples were wrapped in clean aluminum foils. They were then placed in

clean zip lock bags. The sediment samples, directly after collection, were kept in a refrigerator prior to laboratory analysis.

2.3) Vegetable sample

Vegetable samples were collected two areas including the production farm areas beside Wang River (site a) and the fresh market (site b) in Lampang Province (September 2018–May 2019). From this initial study, the 20 species of vegetable samples were chosen for extraction and analysis as presented in Table 1. Samples are to be analyzed within 3 d of sample receipt or 4 days of sample pickup. Samples are kept at 4 °C before analysis to prevent the disappearance or degradation of pesticide residues.

Table 1 Preliminary pesticide toxicity screening of twenty species of vegetable samples

Scientific name	Common name	Sites
<i>Zea mays</i> L.	Corn	a
<i>Mentha cordifolia</i> Opiz ex Fresen	Kithen mint	a
<i>Ocimum basilicum</i> L.	Sweet basil	a
<i>Ocimum tenuiflorum</i> L.	Thai basil	a
<i>Apium graveolens</i> L.	Celery	a
<i>Gymnema inodorum</i> (LOUR.) Decne.	Phak Chiang da	a
<i>Brassica oleracea</i> L. var. <i>botrytis</i> L.	Heading broccoli	b
<i>Lactuca sativa</i> L.	Lettuce	b
<i>Vigna unguiculata</i> subsp. <i>sesquipedalis</i>	Yardlong bean	b
<i>Coriandrum sativum</i>	Chinese parsley	b
<i>Brassica alboglabra</i>	Kale	b
<i>Allium cepa</i> var. <i>aggregatum</i>	Onion	b
<i>Raphanus sativus</i> subsp. <i>longipinnatus</i>	Daikon	b
<i>Solanum virginianum</i> L.	Thai eggplant	b
<i>Amaranthus viridis</i>	Green amaranth	b
<i>Daucus carota</i> subsp. <i>sativus</i>	Carrot	b
<i>Capsicum annuum</i>	Chillies	b
<i>Brassica rapa</i> subsp. <i>pekinensis</i>	Chinese cabbage	b
<i>Ipomoea aquatica</i>	Water spinach	b
<i>Brassica oleraceae</i> var. <i>cappitata</i>	Brussels sprouts	b

3) Sample extraction

Regularly, the pesticide residues of concern are present at levels too low for detection. Sample preparation can concentrate the components to adequate amounts for measurement. The extraction, isolation, and concentration of the pesticide residues from vegetables are explained. Analyze the samples unwashed, with the peel intact and, if applicable, stoned. Chop the samples into small pieces using a conventional razor blade. Weigh a 5-g portion of the vegetable samples and place it into an Erlenmeyer flask. Add process control or spiking solutions at this step and let the samples stand at room temperature. The samples were extracted with 5 mL methanol (HPLC grade, Sigma-Aldrich) for 30 min [14, 21–22]. The extracts were filtered through 0.2 µm nylon filters. The extraction sample of residues was transferred into vials and stored at 4 °C in airtight vials before analysis of the quantification of pesticide residues by triple quadrupole GC-MS/MS (Thermo Scientific, USA).

4) Apparatus

The analyses covered the number of substances was approximately 87 compounds. The category of pesticides (Table 2); organophosphate, organochlorine, pyrethroid, and POPs was detected. The quantification of

residues was carried out with gas chromatography triple quadrupole mass spectrometry technique (TSQ 8000 Evo Triple Quadrupole GC-MS/MS, Thermo Scientific, USA). The analytical column used was a TR-Pesticide II (30 m x 0.25 mm, ID 0.25 µm film thickness, Thermo Scientific, USA). The injector temperature was set at 290 °C. The injection volume was 1.0 µL with a splitless mode at 1 min. The initial of the column oven was 80 °C (held for 0.5 min). This temperature was raised at a rate of 15 °C min⁻¹ up to 200 °C; then, the temperature was increased up to 280 °C at a rate of 5 °C min⁻¹ (held for 2 min); and finally, the temperature was increased up to 300 °C at a rate of 5 °C min⁻¹.

Helium at a constant flow rate of 1.0 mL min⁻¹ was used as a carrier gas. Argon was used as collision gas for MS/MS operation at a pressure of 1.5 mTorr. The TSQ 8000 Evo instrument was operated in MS/MS mode using positive electron impact (+EI) in the selected reaction monitoring (SRM) mode. The emission current was set at 50 µA. The transfer line and ion source temperatures were set at 290 °C and 250 °C, respectively. The calibration curves of 87 pesticides obtained indicated excellent sensitivity (0.1 ppb), reproducibility (10% at 5 ppb) and relative standard deviation determined ($R^2 > 0.99$) in the range of 0.1–100 ppb.

Table 2 The categories and types of pesticide substances

The category of pesticides	Types of substances	
Organophosphate	Azinphos ethyl	Formothion
	Azinphos methyl	Iodofenphos
	Bromophos ethyl	Malaoxon
	Bromophos methyl	Malathion
	Bromopropylate	Methacrifos
	Carbophenothion	Methidathion
	Chlorfenvinphos	Mevinphos
	Chlorpyrifos	Monocrotophos
	Chlorpyriphos methyl	Paraaxon ethyl
	Coumaphos	Parathion ethyl
	Diazinon	Parathion methyl
	Dichlofenthion	Phosalone
	Dichlorvos	Phosphamidon

Table 2 The categories and types of pesticide substances (*continued*)

The category of pesticides	Types of substances	
Organophosphate (<i>continued</i>)	Dicrotophos Dimefox Disulfoton Ethion Etrimfos Fenclorophos Fenitrothion Fonofos	Pirimiphos ethyl Pirimiphos methyl Profenophos Propetamphos Pyrazophos Sulfotep Tetrachlorvinphos Triazophos
Organochlorine	Aldrin cis-Chlordane trans-Chlordane Chlorothalonil o,p'-DDD p,p'-DDD o,p'-DDE p,p'-DDE o,p'-DDT p,p'-DDT Dicofol o,p'-Dicofol Dieldrin	alpha-Endosulfan beta-Endosulfan Endosulfan sulfate Endrin HCB alpha-HCH beta-HCH delta-HCH Heptachlor cis-Heptachlor epoxide Lindane Oxychlordane
Pyrethroid	Bifenthrin Cyfluthrin lambda-Cyhalothrin Cypermethrin Deltamethrin Etofenprox Fenpropathrin	Fenvalerate Flucythrinate Fluvalinate Permethrin D-trans-Phenothrin Tetramethrin
POPs	Aldrin cis-Chlordane o,p'-DDT p,p'-DDT Dieldrin Endrin Heptachlor cis-Heptachlor epoxide	Oxychlordane PCB28 PCB52 PCB101 PCB118 PCB138 PCB153 PCB180

5) Pesticide toxicity index

The Pesticide Toxicity Index (PTI) is a screening tool to assess the potential toxicity of multiple pesticide residues. The PTI is the concept based on the concentration addition model to evaluate pesticide toxicity corresponding to Hazard Quotients (HQ). The HQ is used to assess ecological risk according to the guideline of the US.EPA (Figure 2). PTI can also be used to estimate how multiple pesticide residues affect sample quality.

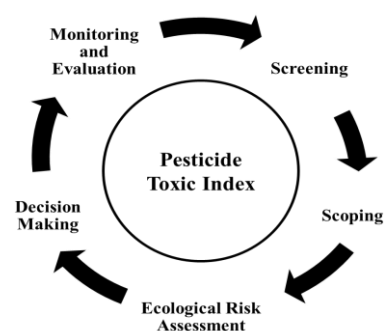


Figure 2 The concept based on the concentration addition model to evaluate the pesticide toxicity index (adapted from US.EPA [23]).

For each type of sample, the Toxicity Quotients (TQ) was computed as the ratio between individual pesticide concentration and maximum residue limits (MRLs). In EU MRLs for pesticides, the chronic and acute dietary consumer exposure to pesticide residues is estimated and provided by European regulations. The TQ is calculated as the sum of ratios between each pesticide residue concentration and the corresponding MRLs [24–25]. The sum of TQ for each sample is the PTI as shown in Eq. 1 [26–29].

$$PTI = \sum_{i=1}^n \frac{C_i}{MRL_{x,i}} = \sum TQ \quad (\text{Eq. 1})$$

Where C_i is the pesticide residue of individual pesticide concentrations (mg kg^{-1}), $MRL_{x,i}$ is the EU maximum residue levels (mg kg^{-1}). To address the risk because of exposure to pesticide mixtures compare with the risk of individual pesticide and to observe the degree of pesticide contamination in each sample as compared to MRLs. The PTI acceptable target with no risk to human health is lower than 1.00.

Result and discussion

1) Pesticide residues in sediment and surface water

The levels of pesticide residues in sediment and surface water from Wang River basin area in 5 sampling points were also investigated in this study (Table 3). The seven chemicals of pesticide residues (Parathion methyl, Methidathion, Bromophos methyl, Chlorfenvinphos, Triazophos, Azinphos ethyl, and D-trans-Phenothrin) were observed in sediment samples from two locations. The level ranged from $12.99\text{--}19.95 \mu\text{g kg}^{-1}$. The highest concentration of D-trans-Phenothrin was found in sediment from Sop Prap location (S2). Interestingly, all of the chemicals, which was found in all sediment samples, was presented in vegetable samples from all locations (farm and market).

The surface water samples were investigated from parameters including total organochlorine pesticides, p,p'-DDT, Alpha-BHC, Dieldrin, Aldrin, Heptachlor, Heptachlor epoxide, and Endrin. The concentration of POPs (Heptachlor, alpha-BHC, Aldrin, Dieldrin, Endrin, p,p'-DDT) was also determined in a water sample from a site close to the farm in the sampling locations. The p,p'-DDT was the lesser contaminant $<0.012 \mu\text{g L}^{-1}$ in samples from Sop Prap location (WA03), whereas Endrin, Dieldrin was found $<0.008 \mu\text{g L}^{-1}$ and Aldrin, alpha-BHC, and Heptachlor in $<0.004 \mu\text{g L}^{-1}$ of samples respectively. The sum of PTI in surface water was detected at 0.4. The value is less than 1.00, so it shows that the surface water is safe and can be used for consumption. The level of all pesticide-contaminated was presented in a surface water sample from only one location (Sop Prap location), with the level lower than the national and international standards permissible limit. Remarkably, all chemicals from sediment and surface water samples were presented in vegetable samples from all locations (farm and market).

2) Pesticide residues in vegetables

Twenty different vegetables include corn, kitchen mint, sweet basil, Thai basil, celery, phak chiang da, heading broccoli, lettuce, yardlong bean, Chinese parsley, kale, onion, daikon, Thai eggplant, green amaranth, Carrot, chillies, Chinese cabbage, water spinach, and Brussels sprouts were obtained from farm and market (September 2018–May 2019). They are the most consumed vegetables in the study area. Many farmers in the area have taken up a vegetable on a commercial basis. The studies covered the determination of 87 pesticides in all vegetable samples as shown in Figure 3.

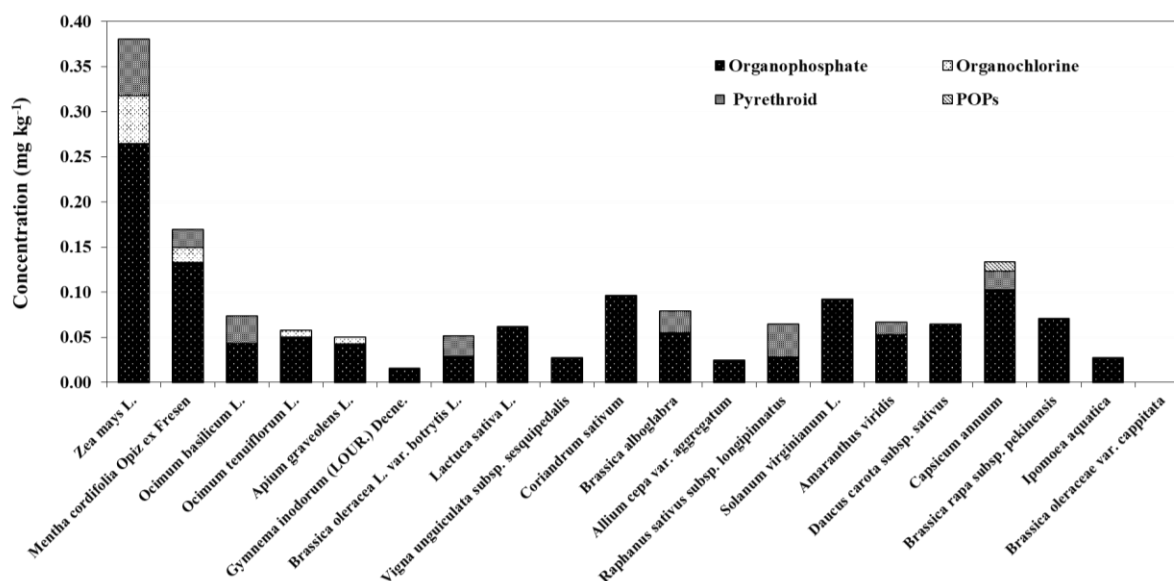
Table 3 Mean of sediment and surface water qualitative parameters of the Wang River

Sample	Station	Pesticide residues	Concentration ($\mu\text{g L}^{-1}$)	National standards ($\mu\text{g kg}^{-1}$)	International standards ($\mu\text{g L}^{-1}$)		TQ
				Thailand [30]	WHO's [31]	EU's ^b [32]	
Sediment ^a	S1	Parathion methyl	15.23	-	-	-	-
		Methidathion	16.70	-	-	-	-
		PTI		-	-	-	-
	S2	Bromophos methyl	12.99	-	-	-	-
		Chlorfenvinphos	14.36	-	-	-	-
		Triazophos	13.70	-	-	-	-
		Azinphos ethyl	16.81	-	-	-	-
		D-trans-Phenothrin	19.95	-	-	-	-
		PTI		-	-	-	-
Surface Water [33]	WA03	Heptachlor	<0.004	0.2	0.03	0.1	0.04
		alpha-BHC	<0.004	0.02	-	0.1	0.04
		Aldrin	<0.004	0.1	0.03	0.1	0.04
		Dieldrin	<0.008	0.1	0.03	0.1	0.08
		Endrin	<0.008	-	-	0.1	0.08
		p,p'-DDT	<0.012	1.0	1.0	0.1	0.12
		PTI		-	-	-	0.40
	WA4.1	N.D.	N.D.	-	-	-	-
	WA5.1	PTI		-	-	-	-
		N.D.	N.D.	-	-	-	-

Note: N.D. Not detected

^a $\mu\text{g kg}^{-1}$

^b The European Community establishes a limit of $0.1 \mu\text{g L}^{-1}$ for individual pesticides and $0.5 \mu\text{g L}^{-1}$ for total pesticides detected. PTI was calculated based on the Official Journal of the European Communities.

**Figure 3** Pesticide groups and concentrations of detection in vegetable samples.

Pesticide residues were detected in 19 analyzed samples (95%) except Brussels sprouts (*Brassica oleracea* var. *cappitata*). The positive of toxicity screening by vegetable samples were most obviously contaminated with organophosphate, accounting for 95% followed by pyrethroid (40%), organochlorine (20%) and POPs (5%), respectively. The frequency of detecting pesticide residues was Coumaphos (12 samples), Mevinphos (9 samples), Triazophos, Azinphos ethyl (5 samples), Dichlorvos, Parathion ethyl, Pirimiphos ethyl, Heptachlor (4 samples), Phosphamidon, Chlorpyrifos methyl, Malathion, Chlorpyrifos, Methidathion, Tetrachlorvinphos, Flucythrinate, Fluvalinate, Bromophos methyl, Methacrifos (3 samples), Dimefox, Formothion, Parathion methyl, o,p'-DDD, Tetramethrin, Formothion, D-trans-Phenothrin, Diazinon, Phosalone, Cypermethrin, Pirimiphos methyl, Iodofenphos, Chlorfenvinphos, D-trans-Phenothrin (2 samples), lambda-Cyhalothrin, Fenitrothion, Endrin, beta-Endosulfan, p,p'-DDD, Fonofos, o,p'-DDT, Bifenthrin, Fenpropathrin, Etofenprox, Dicrotophos, Cyfluthrin, and PCB118 (1 sample) as presented in Table 4. The highest pesticide residue concentrations were detected in corn (*Zea mays* L.) 0.38 mg kg⁻¹, followed by kitchen mint (*Mentha cordifolia* Opiz ex Fresen) 0.17 mg kg⁻¹ and chillies (*Capsicum annuum*) 0.13 mg kg⁻¹, respectively. The assessment was based on pesticide residues of individual pesticide concentrations for each vegetable sample. The sample contaminations higher than Codex MRLs for pesticides were not observed.

3) Pesticide toxic index and half-life values

Data on the dissipation in food crops and vegetables is a key aspect of current risk and impact assessment [34]. This is because human exposure to pesticides is generally caused by residues in crops grown for human consumption. Table 4 presents data on the combined health risks posed by the consumption of the vegetable and to human. The hazard indices for the consumption of all vegetables from farms and markets were greater than 1.00. The highest PTI (31.20) was found in corn followed by kitchen mint (16.50) and chillies (11.00) respectively. Half-life is the time required for half of the pesticide to break down [35]. The values of the half-life of pesticides observed in this study are shown range from 1.01 days for Mevinphos to 12.92 days for Dimefox as indicated in Table 4. The highest half-life values "Dimefox" were detected in corn (*Zea mays* L.), chillies (*Capsicum annuum*), and Chinese cabbage (*Brassica rapa* subsp. *pekinensis*). It is therefore important that steps are taken to reduce the levels of pesticide residues on these vegetables. Thorough washing of vegetables and cooking could help eliminate some of these residues. The pesticide risk values for vegetables from all farms and markets were >1.00 and therefore raise concern to the consumer. Pesticide residues could accumulate over a while, and this could have adverse chronic effects on the consumer. There is a critical need to monitor pesticide residues to standardize the amount of pesticide application.

Table 4 Contamination levels detected in vegetable samples collected in Wang River basin area

Common name	Half-Life (day) [36]	Pesticide residues	Concentration (mg kg ⁻¹)	MRLs (mg kg ⁻¹)		TQ
				Codex [37]	EU [38]	
Corn (<i>Zea mays</i> L.)	12.92	Dimefox	0.01	-	0.01	1.00
	1.12	Dichlorvos	0.01	-	0.01*	1.00
	1.01	Mevinphos	0.02	-	0.01*	2.00
	-	Fonofos	0.01	-	0.01	1.00
	1.80	Formothion	0.02	-	0.01*	2.00

Table 4 Contamination levels detected in vegetable samples collected in Wang River basin area (*continued*)

Common name	Half-Life (day) [36]	Pesticide residues	Concentration (mg kg ⁻¹)	MRLs (mg kg ⁻¹)		TQ
				Codex [37]	EU [38]	
Corn (<i>Zea mays</i> L.) (<i>continued</i>)	3.96	Phosphamidon	0.02	-	0.01*	2.00
	3.27	Chlorpyrifos methyl	0.01	-	0.01*	1.00
	1.61	Parathion methyl	0.01	-	0.01*	1.00
	3.73	Fenitrothion	0.01	6	0.01*	1.00
	2.48	Malathion	0.01	-	0.02*	0.50
	4.01	Chlorpyrifos	0.01	0.05	0.01*	1.00
	2.81	Parathion ethyl	0.01	-	0.05*	0.20
	-	Pirimiphos ethyl	0.01	-	0.01	1.00
	2.86	Methidathion	0.02	-	0.02*	1.00
	-	Tetrachlorvinphos	0.02	-	0.01	2.00
	6.05	Triazophos	0.01	-	0.01*	1.00
	-	Azinphos ethyl	0.02	-	0.02*	1.00
	-	Coumaphos	0.02	-	0.01	2.00
	3.34	Heptachlor	0.01	0.02	0.01*	1.00
	-	o,p'-DDD	0.01	-	0.01	1.00
	2.48	Endrin	0.01	-	0.01*	1.00
	-	beta-Endosulfan	0.01	-	0.05*	0.20
	-	p,p'-DDD	0.01	0.1	0.05*	0.20
	10.78	o,p'-DDT	0.01	0.1	0.05*	0.20
	3.39	Bifenthrin	3.8x10 ⁻³	0.05	0.01*	0.38
	-	Tetramethrin	0.01	-	0.01	1.00
	3.46	Fenpropathrin	3.2 x10 ⁻³	-	0.01*	0.32
	5.78	Flucythrinate	0.02	-	0.01*	2.00
	2.63	Etofenprox	0.01	0.05	0.05	0.20
	2.92	Fluvalinate	0.02	-	0.01*	2.00
				PTI		31.20
Kitchen mint (<i>Mentha cordifolia</i> Opiz ex Fresen)	1.01	Mevinphos	0.02	-	0.01*	2.00
	-	Dicrotophos	0.04	-	0.01	4.00
	1.80	Formothion	0.02	-	0.02*	1.00
	3.96	Phosphamidon	0.02	-	0.01*	2.00
	-	Pirimiphos ethyl	0.01	-	0.01	1.00
	-	Azinphos ethyl	0.02	-	0.02*	1.00
	-	Coumaphos	0.02	-	0.01	2.00
	3.34	Heptachlor	0.01	-	0.01*	1.00
	-	o,p'-DDD	0.01	-	0.01	1.00
	5.78	Flucythrinate	0.01	-	0.02*	0.50
	2.92	Fluvalinate	0.01	-	0.01*	1.00
				PTI		16.50

Table 4 Contamination levels detected in vegetable samples collected in Wang River basin area (*continued*)

Common name	Half-Life (day) [36]	Pesticide residues	Concentration (mg kg ⁻¹)	MRLs (mg kg ⁻¹)		TQ
				Codex [37]	EU [38]	
Sweet basil (<i>Ocimum basilicum</i> L.)	1.01	Mevinphos	0.02	-	0.01*	2.00
	-	Pirimiphos ethyl	0.01	-	0.01	1.00
	-	Coumaphos	0.02	-	0.01	2.00
	-	Tetramethrin	0.01	-	0.01	1.00
	5.78	Flucythrinate	0.01	-	0.02*	0.50
	2.92	Fluvalinate	0.01	-	0.01*	1.00
PTI						7.50
Thai basil (<i>Ocimum tenuiflorum</i> L.)	1.01	Mevinphos	0.02	-	0.01*	2.00
	-	Azinphos ethyl	0.02	-	0.02*	1.00
	-	Coumaphos	0.02	-	0.01	2.00
	3.34	Heptachlor	0.01	-	0.01*	1.00
PTI						6.00
Celery (<i>Apium graveolens</i> L.)	3.96	Phosphamidon	0.02	-	0.01*	2.00
	-	Pirimiphos ethyl	0.01	-	0.01	1.00
	-	Coumaphos	0.02	-	0.01	2.00
	3.34	Heptachlor	0.01	-	0.01*	1.00
PTI						6.00
Phak Chiang Da (<i>Gynema inodorum</i> (LOUR.) Decne.)	-	Coumaphos	0.02	-	0.01	2.00
	PTI					2.00
Heading broccoli (<i>Brassica oleracea</i> L. var. <i>botrytis</i> L.)	-	Bromophos methyl	0.01	-	0.01	1.00
	6.05	Triazophos	0.02	-	0.01*	2.00
	4.93	D-trans-Phenothrin	0.02	-	0.02*	1.00
PTI						4.00
Lettuce (<i>Lactuca sativa</i> L.)	1.12	Dichlorvos	0.01	-	0.01*	1.00
	-	Tetrachlorvinphos	0.02	-	0.01	2.00
	6.05	Triazophos	0.01	-	0.01*	1.00
	-	Coumaphos	0.02	-	0.01	2.00
PTI						6.00
Yardlong bean (<i>Vigna unguiculata</i> <i>subsp. sesquipedalis</i>)	1.12	Dichlorvos	0.01	-	0.01*	1.00
	-	Bromophos methyl	0.01	-	0.01	1.00
PTI						2.00
Chinese parsley (<i>Coriandrum sativum</i>)	1.01	Mevinphos	0.02	-	0.02*	1.00
	-	Methacrifos	0.01	-	0.05*	0.20
	2.16	Diazinon	0.01	-	5	2x10 ⁻³
	3.27	Chlorpyrifos methyl	0.01	-	1	0.01
	2.48	Malathion	0.01	-	0.02*	0.50
	4.01	Chlorpyrifos	0.01	-	5	2x10 ⁻³
	-	Coumaphos	0.02	-	0.01	2.00
PTI						3.71

Table 4 Contamination levels detected in vegetable samples collected in Wang River basin area (*continued*)

Common name	Half-Life (day) [36]	Pesticide residues	Concentration (mg kg ⁻¹)	MRLs (mg kg ⁻¹)		TQ
				Codex [37]	EU [38]	
Kale (<i>Brassica alboglabra</i>)	1.12	Dichlorvos	0.01	-	0.01*	1.00
	-	Methacrifos	0.01	-	0.01*	1.00
	3.27	Chlorpyrifos methyl	0.01	-	0.01*	1.00
	4.72	Phosalone	0.02	-	0.01*	2.00
	2.86	lambda-Cyhalothrin	0.01	0.5	0.01	1.00
	4.24	Cypermethrin	0.02	1	0.01	2.00
				PTI		8.00
Onion (<i>Allium cepa</i> var. <i>aggregatum</i>)	2.81	Parathion ethyl	0.01	-	0.05*	0.20
	-	Coumaphos	0.02	-	0.01	2.00
				PTI		2.20
Daikon (<i>Raphanus sativus</i> subsp. <i>longipinnatus</i>)	1.61	Parathion methyl	0.02	-	0.01*	2.00
	-	Bromophos methyl	0.01	-	0.01	1.00
	4.93	D-trans-Phenothrin	0.02	-	0.02*	1.00
	4.24	Cypermethrin	0.01	0.01	0.05*	0.20
				PTI		4.20
Thai eggplant (<i>Solanum virginianum</i> L.)	1.01	Mevinphos	0.02	-	0.01*	2.00
	1.61	Parathion methyl	0.02	-	0.01*	2.00
	2.16	Pirimiphos methyl	0.01	-	0.01*	1.00
	2.48	Malathion	0.01	-	0.02*	0.50
	2.86	Methidathion	0.02	-	0.02*	1.00
	-	Coumaphos	0.02	-	0.01	2.00
				PTI		8.50
Green amaranth (<i>Amaranthus viridis</i>)	2.16	Diazinon	0.01	0.5	0.01*	1.00
	2.81	Parathion ethyl	0.01	-	0.05*	0.20
	4.72	Phosalone	0.02	-	0.01*	2.00
	-	Coumaphos	0.02	-	0.01	2.00
	2.39	Cyfluthrin	0.01	-	0.01	1.00
				PTI		6.20
Carrot (<i>Daucus carota</i> subsp. <i>sativus</i>)	1.01	Mevinphos	0.02	-	0.01*	2.00
	2.86	Methidathion	0.02	-	0.02*	1.00
	-	Tetrachlorvinphos	0.02	-	0.01	2.00
	-	Iodofenphos	0.01	-	0.01	1.00
				PTI		6.00
Chillies (<i>Capsicum annum</i>)	12.92	Dimefox	0.01	-	0.01	1.00
	1.01	Mevinphos	0.02	-	0.01*	2.00
	10.20	Chlorfenvinphos	0.01	-	0.01*	1.00
	-	Iodofenphos	0.01	-	0.01	1.00
	6.05	Triazophos	0.01	-	0.01*	1.00
	-	Azinphos ethyl	0.02	-	0.02*	1.00
	-	Coumaphos	0.02	-	0.01	2.00

Table 4 Contamination levels detected in vegetable samples collected in Wang River basin area (*continued*)

Common name	Half-Life (day) [36]	Pesticide residues	Concentration (mg kg ⁻¹)	MRLs (mg kg ⁻¹)		TQ
				Codex [37]	EU [38]	
Chillies (<i>Capsicum annuum</i>) (<i>continued</i>)	4.93	D-trans-Phenothrin	0.02	-	0.02*	1.00
	-	PCB118	0.01	-	0.01	1.00
				PTI		11.00
Chinese cabbage (<i>Brassica rapa</i> subsp. <i>pekinensis</i>)	1.01	Mevinphos	0.02	-	0.01*	2.00
	-	Methacrifos	0.01	-	0.01*	1.00
	4.01	Chlorpyrifos	0.01	1	0.01*	1.00
	10.20	Chlorfenvinphos	0.01	-	0.01*	1.00
	-	Azinphos ethyl	0.02	-	0.02*	1.00
				PTI		6.00
Water spinach (<i>Ipomoea</i> <i>aquatica</i>)	2.16	Pirimiphos methyl	0.01	-	0.01	1.00
	6.05	Triazophos	0.01	-	0.01*	1.00
				PTI		2.00
Brussels sprouts (<i>Brassica</i> <i>oleraceae</i> var. <i>cappitata</i>)	-	N.D.	N.D.	-	-	-
				PTI		-

Note: N.D. Not detected

*The EU applies a general default MRLs of 0.01 mg kg⁻¹ for any active substance/commodity combination where MRLs is not specifically established

Conclusion

This study aimed to evaluate the presence of pesticide residues in vegetables, surface water, and sediment obtained from the river basin area. The results show that the concentration of pesticides in sediment samples is between 12.99–19.95 µg kg⁻¹ but MRLs of detection chemicals were not defined in the sediment quality guidelines in surface water for Thailand. The PTI was detected at 0.4 in the sum of surface water samples. This means that the surface water is safe and can be used for consumption. Furthermore, the hazards indices for the consumption of all vegetables were greater than 1.00. The highest PTI (31.20) was found in corn followed by mint (16.50) and chilies (11.00) respectively. Consumption of these vegetables could present a potential health risk associated with pesticide residues. Responses to quality of care concerns must be taken because pesticide contamination could

accumulate and pose long term effects on consumer health. There is a critical need to monitor pesticide residues to standardize the amount of pesticide application. Enforcing the laws on the use of pesticides in order to improve measures to reduce the levels of pesticide contaminated and their corresponding health risks.

References

- [1] Fenik, J., Tankiewicz, M., Biziuk, M. Properties and determination of pesticides in fruits and vegetables. *TrAC Trends in Analytical Chemistry*, 2011, 30, 814–826.
- [2] Mahmood, I., Imadi, S.R., Shazadi, K., Gul, A., Hakeem, K.R. Effects of pesticides on environment. In: Hakeem, K.R., Akhtar, M.S., Abdullah, S.N.A. *Plant, soil and microbes*. Cham: Springer, 2016, 253–269.

- [3] Speck-Planche, A., Kleandrova, V.V., Scotti, M.T. Fragment-based approach for the silico discovery of multi-target insecticides. *Chemometrics and Intelligent Laboratory*, 2012, 111, 39–45.
- [4] Tadevosyan, N.S., Poghosyan, S.B., Khachatryan, B.G., Muradyan, S.A., Guloyan, H.A., Tshantshapanyan, A.N., Tadevosyan, A.E. Residues of xenobiotics in the environment and phytotoxic activity in armenia. *Journal of Environmental Science and Health, Part A*, 2019, 54, 1011–1018.
- [5] Feng, J.F., Tang, H., Chen, D., Li, L. Monitoring and risk assessment of pesticide residues in tea samples from china. *Human and Ecological Risk Assessment*, 2015, 21, 169–183.
- [6] Lozowicka, B., Rutkowska, E., Jankowska, M., Hrynko, I., Kaczynski, P. Toxicological evaluation of multi-class pesticide residues in vegetables and associated human health risk study for adults and children. *Human and Ecological Risk Assessment*, 2016, 22, 1480–1505.
- [7] Yazgan, M.S., Tanik, A. A new approach for calculating the relative risk level of pesticides. *Environment International*, 2005, 31, 687–692.
- [8] Ngowi, A.V.F., Mbise, T.J., Ijani, A.S.M., London, L., Ajayi, O.C. Pesticides use by smallholder farmers in vegetable production in Northern Tanzania. *Crop Protection*, 2007, 26, 1671–1624.
- [9] Gill, H.K., Garg, H. Pesticides: Environmental impacts and management strategies. In: Larramendy, M.L., Soloneski, S. *Pesticide Toxic-Aspects*. London: IntechOpen., 2014. 187–230.
- [10] Alavanja, M.C.R., Ross, M.K., Bonner, M.R. Increased cancer burden among pesticide applicators and others due to pesticide exposure. *CA: A Cancer Journal for Clinicians*, 2013, 63, 120–142.
- [11] Malhat, F.M., El Sharkawi, H.M., Loutfy, N.M., Ahmed, M.T. Field dissipation and health hazard assessment of Fenhexamid on Egyptian grapes. *Toxicological and Environmental Chemistry*, 2014, 96, 722–729.
- [12] Yazgan, M.S., Tanik, A. A new approach for calculating the relative risk level of pesticides. *Environment International*, 2005, 31, 687–692.
- [13] Ahoudi, H., Gnandi, K., Tanouayi, G., Ouro-Sama, K., Yorke, J-C., Creppy, E.E., Moeshch, C. Assessment of pesticides residues contents in the vegetables cultivated in urban area of Lome (southern Togo) and their risks on public health and the environment, Togo. *International Journal of Biological and Chemical Science*, 2018, 12, 2172–2185.
- [14] Lee, S-J., Mehler, L., Beckman, J., Diebolt-Brown, B., Prado, J., Lackovic, M., Calvert, G.M. Acute pesticide illnesses associated with off-target pesticide drift from agricultural applications: 11 states, 1998–2006. *Environmental Health Perspectives*, 2011, 119, 1162–1169.
- [15] PAN Germany. Pesticide and health hazards-facts and figures, 2012. [Online] Available from: http://www.pan-germany.org/download/Vergift_EN-201112-web.pdf [Accessed 9 September 2019].
- [16] World Health Organization. The world health report 2002. Reducing risks, promoting healthy life. WHO. Geneva [Online] Available from: https://www.who.int/whr/2002/en/whr02_en.pdf?ua=1 [Accessed 10 March 2020]
- [17] Hossain, M.S., Fakhruddin, A.N.M., Chowdhury, M.A.Z., Rahman, M.A., Alam, M.K. Health risk assessment of selected pesticide residues in locally produced vegetables of Bangladesh. *International Food Research Journal*, 2015, 22, 110–115.

- [18] Bureau of Occupational and Environmental Diseases (BOED), Annual report 2018, Nonthaburi. [Online] Available from: <http://envocc.ddc.moph.go.th/contents?g=4&s=1> [Accessed 9 September 2019].
- [19] Komsai, A., Liengcharernsit, W., Kinouchi, T. Development of flood routing models for wang river basin. *ASEAN Engineering Journal Part C*, 2014, 4, 16–29.
- [20] Noicharoen, D., Parkpian, P., Shipin, O.V., Polprasert, C., DeLaune, R.D., Kongchum, M. Effect of salinity on adsorption and desorption of paraquat in pak phanang river sediment, Thailand. *Journal of Environmental Science and Health, Part A*, 2012, 47, 1897–1908.
- [21] Ochiai, N., Sasamoto, K., Kanda, H., Yamagami, T., David, F., Tienpont, B., Sandra, P. Optimization of a multi-residue screening method for the determination of 85 pesticides in selected food matrices by stir bar sorptive extraction and thermal desorption GC-MS. *Journal of Separation Science*, 2005, 28, 1083–1092.
- [22] Obana, H., Okihashi, M., Akutsu, K., Kitagawa, Y., Hori, S. Determination of neonicotinoid pesticide residues in vegetables and fruits with solid phase extraction and liquid chromatography mass spectrometry. *Journal of Agricultural and Food Chemistry*, 2003, 51, 2501–2505.
- [23] United States Environmental Protection Agency. Guidelines for ecological risk assessment. EPA/630/R-95/002F. Washington, DC. 1998. [Online] Available from: https://www.epa.gov/sites/production/files/2014/11/documents/eco_risk_assessment1998.pdf [Accessed 12 July 2019].
- [24] Mac Loughlin, T.M., Leticia Peluso, M., Agustina Etchegoyen, M., Alonso, L.L., Cecilia de Castro, M., Cecilia Percudani, M., Marino, D.J.G. Pesticide residues in fruits and vegetables of the argentine domestic market: Occurrence and quality. *Food Control*, 2018, 93, 129–138.
- [25] Ramadan, M.F.A., Abdel-Hamid, M.M.A., Altorgoman, M.M.F., AlGaramah, H.A., Alawi, M.A., Shati, A.A., Shweeta, H.A., Awwad, N.S. Evaluation of pesticide residues in vegetables from Asir Region, Saudi Arabia. *Molecules*, 2020, 25, 205.
- [26] Belden, J.B., Gilliom, R.J., Martin, J.D., Lydy, M.J. Relative toxicity and occurrence patterns of pesticide mixtures in streams draining agricultural watersheds dominated by corn and soybean production. *Integrated Environmental Assessment and Management*, 2007, 3, 90–100.
- [27] Nowell, L.H., Norman, J.E., Moran, P.W., Martin, J.D., Stone, W.W. Pesticide toxicity index- A tool for assessing potential toxicity of pesticide mixtures to freshwater aquatic organisms. *Science of the Total Environment*, 2014, 476–477, 144–157.
- [28] Munn, M.D., Gilliom, R.J. Pesticide toxicity index for freshwater aquatic organisms. *Water-Resources Investigations Report 01-4077*. Reston, VA. 2001. [Online] Available from: <https://pubs.usgs.gov/wri/wri014077/wri014077.pdf> [Accessed 12 July 2019].
- [29] Munn, M.D., Gilliom, R.J., Moran, P.W., Nowell, L.H. Pesticide toxicity index for freshwater aquatic organisms, (2nd ed.), *Scientific Investigations Report 2006-5148*. Reston, VA. 2006. [Online] Available from: https://pubs.usgs.gov/sir/2006/5148/sir_2006-5148.pdf [Accessed 12 July 2019].
- [30] Pollution Control Department. Sediment quality guidelines in surface water for Thailand. [online] Available from:

- <http://www.pcd.go.th/file/17Aug2018.pdf> [Accessed 1 March 2020].
- [31] World Health Organization. Guidelines for drinking-water quality: Fourth edition incorporating the first addendum. [Online] Available from: <https://apps.who.int/iris/bitstream/handle/10665/254637/9789241549950-eng.pdf;jsessionid=54F740622E69281150060B34FDCA4819?sequence=1> [Accessed 2 March 2020].
- [32] Official Journal of the European Communities. Council Directive 98/93/EC of 3 November 1998 on the quality of water intended for human consumption. [Online] Available from: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31998L0083&from=EN> [Accessed 2 March 2020].
- [33] Pollution Control Department, Water Quality Management Division. [Online] Available from: <http://iwis.pcd.go.th/index.php?method=service&etc=1590584895100> [Accessed 1 April 2019].
- [34] Fantke, P., Juraske, R. Variability of pesticide dissipation half-lives in plants. *Environmental Science & Technology*, 2013, 47, 3548–3562.
- [35] Bajwa, U., Sandhu, K.S. Effect of handling and processing on pesticide residues in food- A review. *Journal of Food Science and Technology*, 2014, 51, 201–220.
- [36] Fantke, P., Gillespie, B.W., Juraske, R., Jolliet, O. Estimating half-lives for pesticide dissipation from plants. *Environmental Science & Technology*, 2014, 48, 8588–8602.
- [37] Codex International Food Standards. Pesticides residues in food. [Online] Available from: <http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticides/en/> [Accessed 15 August 2019].
- [38] European Commission. EU pesticides database. [Online] Available from: <https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=pesticide.residue.selection&language=EN> [Accessed 15 August 2019].