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Contributed Paper

Removal of Organophosphorus Pesticide Residues in Leaf and Non-leaf Vegetables by Using Ozone Water

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ABSTRACT

Organophosphorus (OPs) pesticides are the most widely used in the group of insecticides to control pests on vegetables and fruits. OPs were detected in vegetables of Thailand exceeding the maximum residue limits. Therefore, the study aims to investigate percentage removal of OPs residues at the difference of ozone levels (600 mg/h and 1,000 mg/h) and the contact times (20, 30, and 40 min) in leaf and non-leaf vegetables. Five types of leaf vegetables were Chinese cabbage, lettuce, kale, parsley and Vietnamese coriander. Five types of non-leaf vegetables were ginger, cucumber, cowpea, broccoli and onion. The results were found that the difference of ozone levels and the contact times had an effect on efficiency of OPs removal in lettuce, kale, and cowpea. Considering average percentage of OPs removal in average contact times of 20-40 min, ozone levels at 1,000 mg/h had the highest percentage of OPs removal in an average of $65.1 \pm 12.4\%$ for leaf vegetables and $78.4 \pm 15.6\%$ for non-leaf vegetables. It can be concluded that the effectiveness of OPs removal in vegetables by using ozone water depended on the chemical structure of OPs residues in vegetables, levels and contact times of ozone and matrix of vegetables.

Keywords: organophosphorus, ozone, vegetables, pesticides

1. INTRODUCTION

Vegetables are important part of healthy diet and provide several nutrients, including vitamins, potassium and fibers. On the other hand, farmers use pesticides for killing pests and improving agricultural productivity. Organophosphorus (OPs) pesticides are the

most widely used in the group of insecticides to control pests on vegetables and fruits.

OPs were detected in vegetables of Thailand and detected exceeding the maximum residue limits (MRL). The study of Sappamrer and Hongsibsong [1] investigated

OP residues in vegetables from farms, markets, and a supermarket, Phayao Province of northern Thailand. They found the most common OP pesticides detected in farm samples were chlorpyrifos, malathion, monocrotophos, diazinon, omethoate, and dicrotophos. The most common OP pesticides detected in market samples were chlorpyrifos, diazinon, parathion-methyl, profenofos, primiphos-ethyl, and fenitrothion. The OP pesticides detected in supermarket samples were chlorpyrifos, and diazinon. In addition, they found that 59.3% of samples from farms and 13.2% from markets had OP residues above the MRL. Wanwimolruk et al [2]. investigated pesticide residues in Chinese kale, pakchoi and morning glory from local markets and supermarkets in Thailand. The results were found that 48% (local markets) and 35% (supermarkets) for Chinese kale; 71% (local markets) and 55% (supermarkets) for pakchoi; and 42% (local markets) and 49% (supermarkets) for the morning glory had pesticide residues exceeding the MRL. The continuous use of pesticides causes adverse effects on ecosystem and human health [2]. Acute toxicity of OPs occurs by inhibiting acetylcholinesterase of the nervous system, which leads to the excess of acetylcholine (ACh), and interferes with the nerve impulse transmission at nerve endings. The poisoning symptoms included salivation, excessive sweating, nausea, vomiting, abdominal cramp, headache and weakness [3]. Epidemiological studies also suggested that exposure to OPs had an effect on neurodevelopment and adverse health outcomes on childhood, neurological disorders and DNA damage on adults [4,5].

There are several conventional methods for removing OPs residues in vegetable such as washing with tap water, salt solution, tamarind solution and baking soda. The study of Harinathareddy et al.[6] reported that

efficiency of OPs removal in tomato samples was 37-73.2% for tap water, 42.5-72.3% for lemon water, 26.1-69.1% for 2% tamarind water, 44.3-78.7% for 2% salt solution and 24-65.1% baking soda. Ozone is also alternative to remove pesticides residues from vegetables. Ozone is a potent oxidizing agent which is used for sterilization, deodorization and decomposition of organic matter [7]. It is also able to degrade pesticide structure by free radicals and high pH produced by oxidation process [8]. In addition, ozone does not change the flavor of vegetables; therefore, it is suitable for removing pesticides from vegetables [9, 10]. Ozone was the mostly effectiveness to remove 47.9% of parathion-methyl, 55.3% of parathion, and 53.4% of diazinon for *Brassica rapa* samples at 24 °C and 30 minutes (min) [11]. The highest removal of chlorpyrifos-ethyl was 94.2% for lemon and grapefruit samples [12]. However, other available studies investigated few types of vegetables. Some studies investigated efficiency of ozone treatment for industrials by consideration of temperature, contact time, and bubble size and other factors [11, 13, 14]. Thus, this study aims to study the effectiveness of ozone in removal of OPs residues in vegetables under room condition for domestic application. Percentage removal of OPs residues at the difference of ozone levels (600 and 1,000 mg/h) and at the contact times (20, 30, and 40 min) in leaf and non-leaf vegetables were investigated.

2. MATERIALS AND METHODS

2.1 Vegetable Samples

Ten Vegetable types were chosen for experiments. Five leaf vegetables were Chinese cabbage, lettuce, kale, parsley and Vietnamese coriander. Five non-leaf vegetables were ginger, cucumber, cowpea, broccoli and onion. Five kilograms of each

vegetable sample were purchased from the market of Phayao Province, Northern Thailand.

2.2 Ozone Water

The ozone gas generator was produced by Cyber Air Manufacture (Model CW-1000), Thailand. The ozone gas was bubbled into 3L distilled water at the bottom of cylinder vessel. The selected levels of ozone for bubbling were 600 mg/h and 1,000 mg/h. The air was bubbled into distilled water as a control. The contact times for bubbling ozone and the air were 20-40 min. The dissolved ozone level was determined every 5 min by the Indigo colorimetric method [15].

2.3 Spiking of OPs Standard Before Ozone Treatment

Eighteen OPs standards spiked into the vegetable samples included methamidophos, mevinphos, dicrotophos, monocrotophos, dimethoate, parathion-methyl, fenitrothion, malathion, methidathion, azinphos methyl, diazinon, chlorpyrifos, prothiophos, profenofos, ethion, thriazophos, EPN, and azinphos-ethyl. All OPs standards were purchased from Dr.Ehren-strofer GmbH (Augberg, Germany). The distilled water (1 L) was spiked with 500 mL of OPs stock standard solution (200 mg/mL). The vegetable was immersed into the solution for 2 min under room condition, and then left under room temperature (25-30 °C) for 12 h.

2.4 Ozone Treatment

The vegetable sample spiked with OPs standard (1.5 kilograms) was added into 3 L distilled water in cylinder vessel. The percentage of OPs removal in vegetables was investigated with two different ozone levels (600 and 1,000 mg/h), and three different

contact times (20, 30, and 40 min). The analyses were run in duplicate. The sample in each experiment was finely chopped after treatment with ozone, and randomly taken for OPs analysis of 200 g. All samples were stored at -20 °C until analysis.

2.5 OPs Analysis

The step of sample extraction and analysis were modified from the method of Koesukwiwat et al.[16]. Briefly, 10 mL acetronitrile (HPLC grade, JT baker) and 250 μ L of 5 μ g/mL triphenylphosphate (internal standard, IS) were added with 5 g of vegetable sample, and centrifuged at 2,500 rpm for 5 min. The supernatant was mixed with 6 g of MgSO₄ and 3 g of NaCl, and then centrifuged again at 2,500 rpm for 5 min. The extract was evaporated by using vacuum rotary evaporator (Buchi, Switzerland), and then reconstituted with 5 mL of ethyl acetate (HPLC grade, JT baker). One mL of ethyl acetate was pipetted to dispersive solid phase extraction tube, centrifuged at 2,000 rpm for 3 min, evaporated with gentle stream of nitrogen at room temperature, and then reconstituted in 0.5 mL of ethyl acetate for gas chromatographic (GC) analysis. The GC analysis was carried out on a Hewlett-Packard model 6890 equipped with a flame photometric detector (FPD), a capillary column (DB-5MS, 0.25 mm \times I.D. \times 30 m length \times 0.25 μ m film thickness, Agilent J & W column, Agilent Technologies, USA). GC data were analyzed by using GC Chemstation (Agilent, USA, A.10.02). Temperature programming of the oven was as follows: initial temperature 100 °C for 10 min, first ramp 15 °C/min to 180 °C (5 min), second ramp 5 °C/min to 250 °C (3 min), and the final temperature was maintained at 290 °C for 4 min. Temperature for the injection port was 220 °C (splitless mode), and the carrier gas

was helium 99.999%.

2.6 Quality Control

The quality control of OPs analysis was presented in Table 1. The relative standard deviation coefficient (%RSD) of intrabatch ranged from 2.09% for chlorpyrifos to 48.84% for azinphos-methyl, and % RSD of interbatch ranged from 2.13% for chlorpyrifos to 47.81% for azinphos-methyl. The limit of detection (LOD) and the

limit of quantification (LOQ) ranged between 0.5-2 µg/kg and 1-4 µg/kg, respectively. The linearity relative coefficient (r^2) for all OPs ranged from 0.99326 for azinphos-methyl to 0.9962 for methamidophos. The recoveries of OPs ranged from 43.25% for azinphos-methyl to 132.28% for methamidophos for high spiked level, and ranged from 52.80% for parathion-methyl to 96.38% for diazinon for low spiked level.

Table 1. Quality control of OPs analysis: interbatch, intrabatch, limit of detection, limit of quantification, correlation coefficient, and percentage of recovery.

Organophosphates		Precision (% RSD)		LOD (mg/kg)	LOQ (mg/kg)	R ²	Percentage of recovery	
		Intrabatch (n=5)	Interbatch (n=10)				(n=3)	
							High level	Low level
Methyl group	Methamidophos	6.88	8.11	1	2	0.99962	132.28±2.81	74.56±1.68
	Mevinphos	2.97	4.18	0.5	1	0.99886	126.84±0.77	78.82±1.32
	Dicrotophos	7.87	8.84	1	2	0.99907	125.38±3.68	71.19±3.93
	Monocrotophos	12.18	14.25	2	4	0.99593	115.09±9.37	58.86±3.22
	Dimethoate	12.23	14.59	1	2	0.99945	97.21±9.16	69.68±1.67
	Parathion-methyl	10.39	13.37	1	2	0.99853	95.31±7.13	52.80±4.32
	Fenitrothion	7.68	9.69	1	2	0.99884	100.73±5.77	61.79±3.25
	Malathion	4.99	7.23	1	2	0.99894	112.83±2.67	69.18±0.85
	Methidathion	11.80	11.96	1	2	0.99822	98.01±12.88	73.76±0.56
Azinphos-methyl	48.84	47.81	2	4	0.99326	43.25±27.24	-	
Ethyl group	Diazinon	3.10	2.39	0.5	1	0.99853	124.23±1.48	96.38±1.92
	Chlorpyrifos	2.09	2.13	1	2	0.99782	118.33±0.75	83.18±1.39
	Prothiophos	3.70	2.93	0.5	1	0.99783	121.93±1.14	83.06±0.99
	Profenofos	7.46	8.47	1	2	0.99866	119.65±4.74	65.36±1.73
	Ethion	2.59	3.20	0.5	1	0.99795	119.82±1.13	89.02±1.41
	Triazophos	6.41	8.64	1	2	0.99884	136.59±4.29	68.48±2.19
	EPN	4.05	4.64	1	2	0.99707	117.43±3.60	56.11±1.60
	Azinphos-ethyl	10.65	12.38	1	2	0.99916	108.00±7.17	60.02±3.63

%RSD = percentage of relative standard deviation, LOD = Limit of detection, LOQ = Limit of quantification, R² = correlation coefficient, mg/kg = microgram per kilogram.

2.7 Statistical Analysis

The percentage of OPs removal was expressed as mean and standard deviation (SD). The statistical differences of dissolved ozone levels of ozone water between ozone producing and contact time were

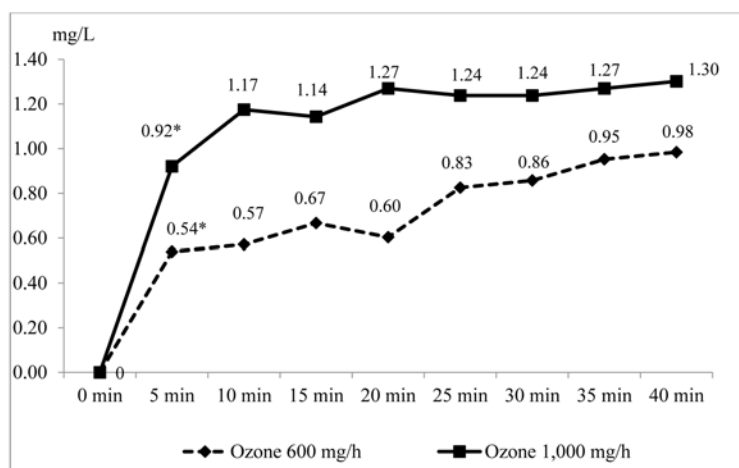
tested by using Mann-whitney U test at P value < 0.05. The statistical differences of OPs removal percentage between treatments were tested by using one-way ANOVA and t-test at P value < 0.05.

3. RESULTS AND DISCUSSION

3.1 Dissolved Ozone Levels of Ozone Water

Figure 1 presents the dissolved ozone levels of ozone water which were produced by bubbling ozone at 600 and 1,000 mg/h. Bubbling of ozone at 600 mg/h produced

dissolved ozone levels of 0.54 mg/L for 5 min, 0.57 mg/L for 10 min, 0.67 mg/L for 15 min, 0.60 mg/L for 20 min, 0.83 mg/L for 25 min, 0.86 mg/L for 30 min, 0.95 mg/L for 35 min, and 0.98 mg/L for 40 min. Dissolved ozone levels at 5 min were significantly higher than those at 0 min.



* Dissolved ozone levels at 5 min were significantly higher than those at 0 min, ** Dissolved ozone levels at 25 min were significantly higher than those at 20 min

Figure 1. Dissolved ozone levels (mg/L) at ozone gas production of 600 and 1,000 mg/h.

Bubbling of ozone at 1,000 mg/h produced dissolved ozone levels of 0.92 mg/L for 5 min, 1.17 mg/L for 10 min, 1.14 mg/L for 15 min, 1.27 mg/L for 20 min, 1.24 mg/L for 25 min, 1.24 mg/L for 30 min, 1.27 mg/L for 35 min, and 1.30 mg/L for 40 min. Dissolved ozone levels at 25 min were significantly higher than those at 20 min. The remarkable findings were that dissolved ozone levels at 1,000 mg/h in each specified time were significantly higher than those at 600 mg/h. It can be concluded that dissolved ozone levels were related proportionally with ozone gas production. In addition, the dissolved ozone levels increased rapidly, and then increased slightly and stabilized at the ozone saturation levels [17].

3.2 Types of OPs Removal in Vegetable Samples by Ozone

Table 2 shows the types of OPs removal in vegetables by using ozone. The first three ranks of OPs that can remove by using ozone were methamidophos, monocrotophos, and dimethoate, respectively. It is possible that all of these chemicals were aliphatic OPs. The chemical structure of aliphatic OPs was easier degradation than those of phenyl and heterocyclic OPs. There are two pathways of chemical degradation including molecular and radical pathways. The molecular pathway occurs via direct reaction of ozone molecules with unsaturated and aromatic hydrocarbons with -OH, -CH₃, and -NH₂ groups. The radical pathway occurs via reaction of decomposition of ozone with aliphatic

hydrocarbon and chlorinated hydrocarbons [18,19]. Therefore, OPs molecule that involved phosphorus atom might be broken, replaced with oxygen atom, and formed to

simple esters of phosphoric acids. In addition, the main reaction for OPs molecule with P=S group was taken place from P=S bonds to P=O bonds [18, 20, 21].

Table 2. Types of OPs removal in vegetables by ozone.

Vegetables		Methamidophos	Mevinphos	Dicrotophos	Monocrotophos	Dimethoate	Parathion-methyl	Fenitrothion	Metidathion	Asinphos-methyl	Diazinon	Chlorpyrifos	Profenofos	Ethion	Triazophos	EPN	Azinphos-ethyl
Leaf vegetables																	
	Chinese cabbage	√	√		√	√	√	√	√		√				√		√
	Lettuce	√	√	√	√	√		√			√						√
	Kale	√			√	√	√	√	√		√				√	√	√
	Parsley	√		√	√	√											
	Vietnamese Coriander	√			√	√											
Non-leaf vegetables																	
	Ginger	√										√	√	√	√	√	√
	Cucumber			√	√							√	√	√		√	
	Cow pea	√			√	√									√		√
	Broccoli			√			√					√					
	Onion	√		√													√
	No. of vegetable types	8	2	5	7	6	3	3	2	0	3	3	2	2	4	4	5

3.3 Percentage of OPs Removal at Difference of Ozone Levels and Contact Times

Table 3 and Table 4 show the percentage of OPs removal at the difference of ozone levels and contact times in leaf and non-leaf vegetables. The difference of ozone levels and contact times had an effect on OPs removal in lettuce, kale, and cowpea.

In lettuce, the percentage of OPs removal at 600 mg/h of ozone levels was 58.7±16.5% for 20 min, 57.8±21.0% for 30 min, and 62.7±24.8% for 40 min. The percentage of OPs removal at 1,000 mg/h of ozone levels was 62.7±24.6% for 20 min, 74.7±21.0% for 30 min, and 77.9±16.3% for 40 min. The percentage of OPs removal by distilled

water (control) was 71.8±19.9% for 20 min, 37.4±10.9% for 30 min, and 46.7±23.4% for 40 min. Considering ozone levels on OPs removal, ozone levels at 1,000 mg/h for 30 and 40 min had significantly higher percentage of OPs removal than distilled water (P value=0.002 and 0.032, respectively).

In kale, the percentage of OPs removal at 600 mg/h of ozone levels was 69.6±21.2% for 20 min, 77.3±17.7% for 30 min, and 58.4±25.5% for 40 min. The percentage of OPs removal at 1,000 mg/h of ozone levels was 76.3±17.2% for 20 min, 77.0±20.4% for 30 min, and 85.1±14.4% for 40 min. The percentage of OPs removal by distilled water (control) was 62.6±23.8% for 20 min,

69.7±26.5% for 30 min, and 65.1±22.8% for 40 min. Considering ozone levels on OPs removal, ozone levels at 1,000 mg/h for 40 min had significantly higher percentage of OPs removal than ozone levels at 600 mg/h (P value=0.025).

Table 3. Percentage of OPs removal at difference of ozone levels and contact times in leaf vegetables.

Vegetable type	Ozone levels, mg/h.	Percentage of OPs removal in various contact time (%) ^Σ				
		20 min ^d	30 min ^c	40 min ^f	Average ^x	P value
Chinese cabbage	1,000 mg/h (n=10)	64.7±21.3	81.6±18.2	62.6±24.0	69.6±22.3	0.110
	600 mg/h (n=10)	69.2±18.8	78.1±18.6	60.4±35.1	69.2±25.6	0.311
	Distilled water (n=10)	69.4±22.8	74.1±20.2	68.7±19.9	70.7±20.4	0.819
	P value	0.853	0.682	0.780	0.949	
Lettuce	1,000 mg/h (n=8) ^a	62.7±24.6	74.7±21.0	77.9±16.8	71.8±16.3	0.333
	600 mg/h (n=8) ^b	58.7±16.5	57.8±21.0	62.7±24.8	59.7±20.0	0.884
	Distilled water (n=8) ^c	71.8±19.9	37.4±10.9	46.7±23.4	52.0±12.7	0.004 ^{de,df**}
	P value	0.440	0.002 ^{ac**}	0.032 ^{ac*}	0.78	
Kale	1,000 mg/h (n=10) ^a	76.3±17.2	77.0±20.4	85.1±14.4	79.5±16.5	0.467
	600 mg/h (n=10) ^b	69.6±21.2	77.3±17.7	58.4±25.5	68.4±19.6	0.165
	Distilled water (n=10) ^c	62.6±23.8	69.7±26.5	65.1±22.8	65.8±21.9	0.808
	P value	0.356	0.682	0.025 ^{ab*}	0.267	
Parsley	1,000 mg/h (n=4)	59.0±18.7	46.2±18.4	56.5±17.7	53.9±17.9	0.592
	600 mg/h (n=4)	61.8±13.2	66.2±22.8	64.0±14.8	64.0±13.3	0.938
	Distilled water (n=4)	58.1±22.2	59.8±27.0	40.6±17.7	52.8±19.5	0.447
	P value	0.957	0.482	0.189	0.612	
Vietnamese Coriander	1,000 mg/h (n=3)	51.8±21.5	43.4±17.7	56.3±9.0	50.5±13.3	0.658
	600 mg/h (n=3)	32.2±25.2	36.6±21.2	47.6±12.7	38.8±19.2	0.655
	Distilled water (n=3)	43.6±9.5	36.7±26.7	38.9±21.5	39.8±18.0	0.917
	P value	0.518	0.913	0.434	0.667	

* P value < 0.05, ** P value < 0.01, ^a = ozone levels at 1,000 mg/h, ^b = ozone levels at 600 mg/h, ^c = distilled water (control), ^d = contact time 20 min, ^e = contact time 30 min, ^f = contact time 40 min, ^x = % of average OPs removal in average contact times of 20-40 min, ^Σ = summation of percentage of OPs removal.

Table 4. Percentage of OPs removal at difference of ozone levels and contact times in non-leaf vegetables.

Vegetable type	Ozone levels, mg/h.	Percentage of organophosphate removal in various contact time (%) ^Σ				
		20 min ^d	30 min ^e	40 min ^f	Average ^x	P value
Ginger	1,000 mg/h (n=7)	88.6±19.9	93.0±15.9	94.0±9.1	91.9±12.9	0.788
	600 mg/h (n=7)	97.4±4.2	96.0±8.0	89.1±26.1	94.2±12.8	0.593
	Distilled water (n=7)	78.1±20.0	90.4±15.1	80.1±22.2	82.9±16.6	0.455
	P value	0.118	0.747	0.448	0.314	
Cucumber	1,000 mg/h (n=6)	88.1±17.1	73.7±20.3	86.6±16.5	82.8±12.5	0.342
	600 mg/h (n=6)	72.6±28.1	62.1±25.6	87.1±16.8	73.9±20.2	0.225
	Distilled water (n=6)	73.1±38.3	65.6±35.1	83.5±28.1	74.1±29.0	0.668
	P value	0.589	0.761	0.949	0.723	
Cowpea	1,000 mg/h (n=5) ^a	47.2±33.2	90.9±11.8	92.6±11.0	76.9±17.5	0.008 ^{de,df**}
	600 mg/h (n=5) ^b	92.2±9.3	48.9±26.9	48.3±25.5	63.1±18.0	0.012 ^{de,df*}
	Distilled water (n=5) ^c	69.8±29.0	76.3±23.2	92.4±10.1	79.5±19.3	0.291
	P value	0.054	0.028 ^{ab*}	0.002 ^{ab, bc**}	0.350	
Broccoli	1,000 mg/h (n=3)	68.8±48.9	98.1±1.6	97.3±2.9	88.0±16.7	0.409
	600 mg/h (n=3)	91.2±13.5	93.9±8.8	94.3±8.2	93.1±5.2	0.927
	Distilled water (n=)	98.4±0.9	97.6±2.4	81.2±30.8	92.4±11.4	0.459
	P value	0.478	0.606	0.559	0.846	
Onion	1,000 mg/h (n=3)	67.2±13.7	55.0±38.8	35.0±10.0	52.4±18.9	0.334
	600 mg/h (n=3)	44.4±28.7	60.8±34.9	34.5±22.1	46.5±19.1	0.531
	Distilled water (n=)	41.2±50.9	34.5±34.0	47.6±38.5	41.1±41.1	0.929
	P value	0.628	0.662	0.765	0.889	

* P value < 0.05, ** P value < 0.01, ^a = ozone levels at 1,000 mg/h, ^b = ozone levels at 600 mg/h, ^c = distilled water (control), ^d = contact time 20 min, ^e = contact time 30 min, ^f = contact time 40 min, ^x = % of average OPs removal in average contact times of 20-40 min, ^Σ = summation of percentage of OPs removal.

In cowpea, the percentage of OPs removal at 600 mg/h of ozone levels was 92.2±9.3% for 20 min, 48.9±26.9% for 30 min, and 48.3±25.5% for 40 min. The Percentage of OPs removal at 1,000 mg/h of ozone levels was 47.2±33.2% for 20 min, 90.9±11.8% for 30 min, and 92.6±11.0% for 40 min. The percentage of OPs removal by distilled water (control) was 69.8±29.0% for 20 min, 76.3±23.2% for 30 min, and 92.4±10.1% for 40 min. Considering ozone levels on OPs removal, ozone levels at 1,000 mg/h for 30 min had significantly higher

percentage of OPs removal than ozone levels at 600 mg/h (P value=0.028). Ozone levels at 1,000 mg/h for 40 min and distilled water had significantly higher percentage of OPs removal than ozone levels at 600 mg/h (P value=0.002). Considering contact time of ozone water, ozone levels at 1,000 mg/h for 40 min and 30 min had significantly higher percentage of OPs removal than those for 20 min (P value=0.008). However, ozone levels at 600 mg/h for 20 min had significantly higher percentage of OPs removal than those for 30 min and 40 min (P value=0.012)

In this context, our study shows that ozone levels at 1,000 mg/h (as dissolved ozone levels at 1.3 mg/L) under room condition had the highest efficiency for reducing OPs residues in lettuce, kale, and cowpea at contact times of 30-40 min. The best result was found with the highest contact time (40 min), was effective to remove 77.9% in lettuce, 85.1% in kale, and 92.6% in cowpea. The results, therefore, suggested that the increasing of the ozone levels and the contact times increased removal efficiency of pesticides residues in vegetables. The results were congruent with other studies. Wu et al.[11] reported that dissolved ozone at 1.4 mg/L was an effective to remove 60-99% of 0.1 mg/L diazinon, parathion, parathion-methyl, and cypermethrin in *Brassica rapa* with the contact time of 30 min. Ikuera et al.(2011)[13] reported that the ozone microbubble at two ppm was an effective to remove 33-45% of fenitrothion in lettuce for 10 min. Other studies showed that the temperature, the size of bubble and pH had an effect on efficiency of OPs removal [12,21]. However, our study investigated under room condition because we imitated practical application in household. Besides, ozone is able to degrade pesticide structure by molecular and radical pathways, ozone is also able to against microorganisms by destroying cell walls of organisms [7,8,22]. Therefore, ozone is considered as one of the practical methods for cleaning food products in domestic use.

3.4 Average Percentage of OPs Removal in Average Contact Times of 20-40 min Between Leaf and Non-leaf Vegetables

The average percentage of OPs removal in leaf vegetables was $60.0 \pm 12.5\%$ for 600 mg/h of ozone levels, $65.1 \pm 12.4\%$ for 1,000 mg/h of ozone levels and $56.2 \pm 12.3\%$ for distilled water. The average percentage

in non-leaf vegetables was $74.2 \pm 20.3\%$ for 600 mg/h of ozone levels, $78.4 \pm 15.6\%$ for 1,000 mg/h of ozone levels and $74.0 \pm 19.6\%$ for distilled water (Figure 2). It is likely that the removal efficiency in non-leaf vegetables was higher than those in leaf vegetables. When pesticides were applied, pesticides adhered at vegetable surface and penetrated into insides through cell walls. The structure of cell walls in each type of vegetables was different. However, ozone can remove only pesticides that adhere at the surface of vegetables [11, 23]. The results, therefore, suggested that the matrix of vegetables had an effect on OPs removal by using ozone.

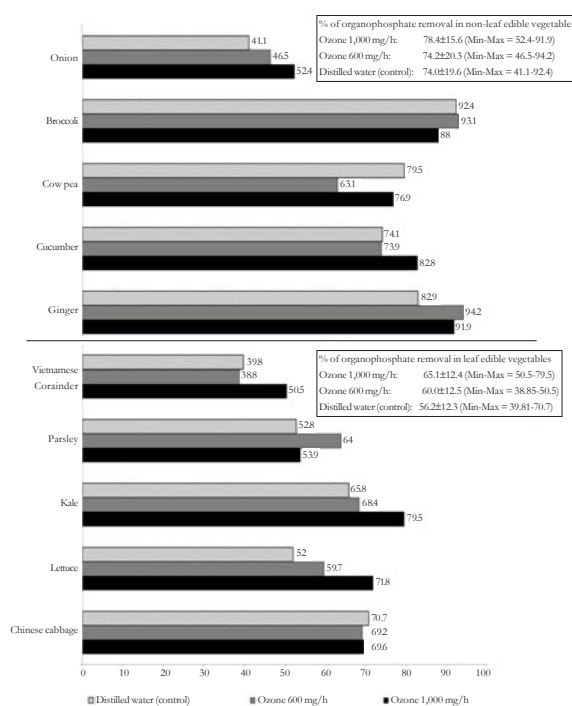


Figure 2. Average percentage of OPs removal in average contact times of 20-40 min.

4. CONCLUSIONS

The overall results indicated that the effectiveness of OPs removal in vegetables by using ozone depended on the chemical structure of OPs residues in vegetables, levels

and contact times of ozone and matrix of vegetables. As a result, ozone levels at 1,000 mg/h, contact times of 40 min, and non-leaf vegetables were the highest effectiveness for removing OPs residues in vegetables. This is challenge for further study of the effectiveness of ozone for removing other pesticides residues in vegetables.

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CONFLICT OF INTEREST

We declare that we have no competing interests.

STATEMENT OF AUTHORSHIP

R. Sapbamrer designed and conducted the study, collected and analyzed the data, and drafted the manuscript. S. Hongsibsong analyzed the pesticides in samples. All authors read and approved the final manuscript.

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