

Field incurred chlorpyrifos and 3,5,6-trichloro-2-pyridinol residues in fresh and processed vegetables

M. Atif Randhawa^{a,*}, F. Muhammad Anjum^a, Anwaar Ahmed^b, M. Saqib Randhawa^c

^a Institute of Food Science and Technology, University of Agriculture, Faisalabad 38040, Pakistan

^b Agricultural Officer, Department of Agriculture Extension, Jauharabad, Khushab, Pakistan

^c Faculty of Agriculture, University of Agriculture, Faisalabad 38040, Pakistan

Received 17 April 2006; received in revised form 16 September 2006; accepted 1 October 2006

Abstract

The effect of washing, peeling and cooking on residue levels of chlorpyrifos and 3,5,6-trichloro-2-pyridinol (TCP) in winter (spinach, cauliflower, potato) and summer vegetables (eggplant, tomato, okra) was determined. Analysis was carried out by capillary gas chromatography (DB-5MS capillary column) with mass selective detection. The samples were collected from trials conducted under controlled conditions as well as from the farmer's field. In supervised field trials, the highest chlorpyrifos residue was found at raw stage in spinach (1.87 mg kg⁻¹) followed by okra (1.41 mg kg⁻¹) and eggplant (1.25 mg kg⁻¹). The lowest residue of chlorpyrifos was recorded in cauliflower (0.036 mg kg⁻¹). The chlorpyrifos residue reduced from 15 to 33% after washing, 65–85% post-peeling and cooking further lowered it from 12% to 48% in all the tested vegetables; while an increase in TCP concentration was observed during heat treatment. Out of 267 vegetable samples collected from the farmer's field, 225 samples contained detectable residues representing 84% rate of contamination. About 6% of samples contained chlorpyrifos residues above maximum residue limits (MRLs). However, vegetable processing reduced the chlorpyrifos residue below the MRL.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Chlorpyrifos; TCP; Vegetables; Household processing; Supervised field trial; Farmer field

1. Introduction

Good knowledge of the pesticide fate in agriculture is necessary to properly assess human exposure and the environmental impact of these contaminants. Chlorpyrifos [*O,O*-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl)phosphorothionate] is an organophosphorus broad spectrum insecticidal active ingredient registered for application to more than 40 different food commodities. It is a stable compound in neutral and acidic aqueous solutions. Its stability however, decreases as pH increases. It kills insects by disrupting their nervous system and is effective against both sucking and chewing insects and has been widely used to control pests of various vegetables. It is non-systemic, fairly persistent, and highly soluble in organic solvents like acetone, xylene,

and methylene chloride (Anonymous, 2000) but almost insoluble in water (2 mg L⁻¹). Cholinesterase inhibition is the mode of action of chlorpyrifos and is the cause of potential toxicity in human (Oliver, Bolles, & Shurdut, 2000). The acute oral LD₅₀ for rats is 135–163 mg kg⁻¹ (Chattopadhyay, 1993). Suspected effects of chlorpyrifos exposures include birth defects, nervous system disorders and increased rate of leukemia and immune system abnormalities (Mahindru, 2004).

Scientists and food processors have long been interested in the effect of commercial processing on persistence of pesticide residues in food. Early reports by Elkins (1989) and Chin (1991) showed that several canning operations, such as peeling, washing, juice extraction and heat processing, can reduce residue levels in several US crops such as tomatoes, broccoli, green beans and spinach. Recently, Cabras and Angioni (2000) reported the fate of organophosphorus (OP) insecticides and fungicides in grapes, wine and their

* Corresponding author. Tel.: +92 3007677116; fax: +92 419201105.
E-mail address: atifrandhawa@yahoo.com (M.A. Randhawa).

processing products. A study on the degradation of azinphos methyl in fruits showed that residues were detected in apple juice but not in lemon juice (Athanasopoulos & Pappas, 2000). Soliman (2001) pointed out changes in the concentrations of the pesticide residue in potato during washing, peeling and cooking. However, the effect of commercial processing on some economically important agricultural crops of Pakistan, such as cauliflower, okra and eggplant is less known.

Byrne and Pinkerton (2004) examined the effects of common household heat processing on various types of produce. The produce did not contain field incurred residues of chlorpyrifos but was fortified in the laboratory with chlorpyrifos solution. Then both uncooked and cooked samples were analyzed for residues of chlorpyrifos and its metabolite TCP. The results suggested that residues decreased with all of the treatments; however, the sample sizes were too small to apply statistical analysis. These studies are of little practical use to the consumer who wants to know what effect household preparation has upon the field incurred chlorpyrifos and TCP residue levels.

This paper describes the effect of simple household processing techniques on reducing chlorpyrifos and TCP residues in some vegetables.

2. Materials and methods

2.1. Field trials for pesticide

The field trials for the determination of chlorpyrifos residue in winter vegetables: spinach (*Spinacia oleracea* L.), cauliflower (*Brassica oleracea* L.), potato (*Solanum tuberosum* L.) and summer vegetables: eggplant (*Solanum melongena* L.), tomato (*Lycopersicon esculentum* L.) and okra (*Abelmoschus esculentus* L.) were conducted in the field area of The Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan in separate plots measuring 150 × 30 feet each in three replicates. The supervised field plots, received all the routine agronomic practices and the vegetables were sprayed with commercial chlorpyrifos-based product (Larsban 40 EC) at the dose of 6 mL L⁻¹ of water. Keeping in view the pest population, the winter vegetables were sprayed two times, while the summer vegetables were sprayed three times during their growing period and harvested after 7 days of the last spray. The spray was carried out with a Knap-sack hand sprayer in the absence of precipitation and wind.

2.2. Vegetable sampling from the farmer's field

The growers (40–50) of both winter and summer vegetables (spinach, cauliflower, potato, eggplant, tomato and okra) near the city of Faisalabad were selected in each season. They were allowed to grow these vegetables with their normal routine practices. At the time of harvest, all the vegetable samples (6 kg/vegetable/farmer) were collected from the field, brought to laboratory and analyzed on the

same day or if necessary stored at –20 °C after necessary processing as given below till analysis.

2.3. Sample preparation and processing of vegetables

The potato and eggplant samples were hand peeled with stainless steel peeling knife after washing and reduced into slices of suitable size and cooked. Rest of the vegetables (spinach, cauliflower, tomato and okra) were washed and sliced into suitable size and cooked (Fig. 1). All vegetable samples collected from the supervised and farmer's fields were analyzed at three stages i.e. raw, post-washing and after cooking to determine the chlorpyrifos and TCP residue as given below.

(i) *Raw*: The vegetable samples were dry cleaned to remove soil contamination with a disposable paper towel and divided into two groups. One portion was blended in a Warring Blender to make a homogenous sample for subsequent analysis, while other was further processed as under.

(ii) *Washing*: The vegetables were washed by placing in a plastic colander and rinsed under normal tap water for 30 s, with gentle rotation by hand as described by Walter, Arsenault, Pylypiw, and Mattina (2000) and blotted dry with a paper towel and divided into two parts. One portion was analyzed as such after blending in a Warring Blender and the rest was further treated as given below.

(iii) *Cooking*: The vegetables were cooked by using the method of Kilgore and Windham (1970) with following modification: the sliced vegetables were cooked by placing 3/4 cup of water in the sauce pan and adding 1/2 teaspoon of salt. The water was brought to boil and 50 g vegetable was added immediately. The vegetable was covered and cooked for 10–12 min and contents were analyzed for chlorpyrifos and TCP residues.

2.4. Analytical methods and calculations

2.4.1. Sample extraction and cleanup

The residues were extracted from all the samples using the method of Kadenezki et al. (1992) with following modifications: 50 g vegetable was extracted with 50 mL ethyl acetate in the presence of 20 g anhydrous sodium sulphate and 10 g sodium chloride in a Warring Blender at high speed for 3 min. The extract was filtered, transferred directly to a column of Florisil, leaving it to pass through @ 1 mL min⁻¹. The extracts were concentrated on a rotary evaporator at 35 °C just to dryness and redissolved in 10 mL ethyl acetate and cyclohexane (1:1) and filtered through a 0.45 µm filter membrane. Then the sample was subjected to clean up by gel permeation chromatography using a column with Bio-Beads SX-3 (mesh size 200–400) and ethyl acetate–cyclohexane as eluting solvent. The collected elute was reduced to a small volume under a gentle stream of nitrogen gas and analyzed by GC as under.

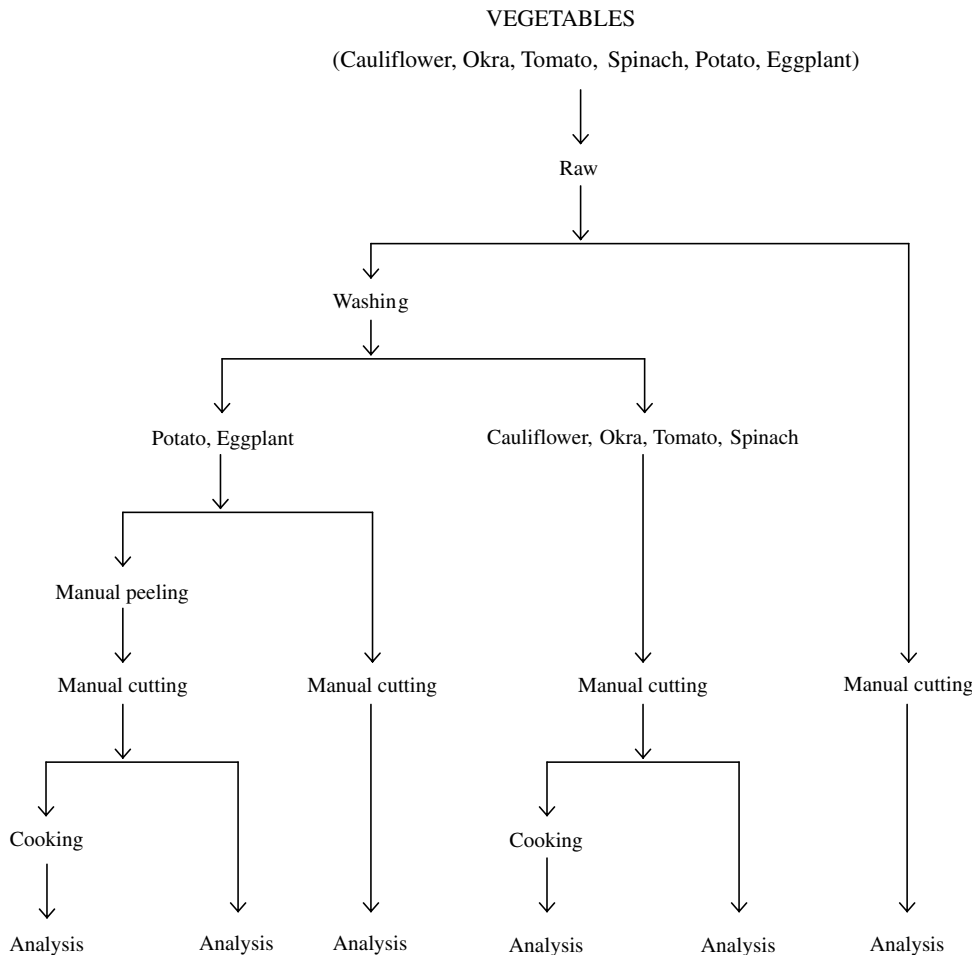


Fig. 1. Processing steps for different vegetables.

2.4.2. Apparatus

After the residues were dried, an internal standard (^{13}C ^{15}N -chlorpyrifos stable isotope) was added, chlorpyrifos was analyzed without derivatization while TCP was derivatized with *N*-methyl-*N*-(*tert*-butyl dimethylsilyl)trifluoroacetamide to form the silyl-dimethyl-*tert*-butyl derivative ($\text{C}_{11}\text{H}_{15}\text{Cl}_3\text{-NOSi}$). Determination was by capillary gas chromatography (DB-5MS capillary column) with mass selective detection, with the mass selective detector using negative chemical ionization and operating in the selective ion mode. The ions that were monitored during the analysis of the crop and water samples were as follows: m/z 313 for chlorpyrifos, m/z 161 for TCP, m/z 318 for $^{13}\text{C}^{15}\text{N}$ -chlorpyrifos (internal standard), m/z 217 for the chlorpyrifos-methyl internal standard for the eggplant samples, and m/z 161 for 2,3,6-TCP (internal standard).

The chlorpyrifos analytical method performance during the study was determined by analysis of freshly fortified control samples ($n = 32$) over the range of 20–9000 ng/sample. The mean recovery was 84% ($s = 9.6\%$). The TCP analytical method performance during the study was determined by analysis of freshly fortified control samples ($n = 40$) over the range of 20–3500 ng/sample. The mean recovery was 86% ($s = 10.7\%$). Both the chlorpyrifos

and the TCP, limit of detection (LOD) and limit of quantitation (LOQ) reported for the study were 5 and 18 ng/sample, respectively (equivalent to 3.33 and 12 ng g^{-1}). The recovery results, as well as the study of LOD and LOQ, indicated that the analytical method was adequate for the quantitation of chlorpyrifos and TCP in the vegetable commodities.

2.5. Statistical analysis

Two parameters were used to report residue levels: mean value and standard deviation from five replicate samples at each sampling point, expressed as mg kg^{-1} . Mean values and standard deviations were calculated and analyzed by Minitab Software Package Version 14.0 (Minitab Inc. State College, PA, USA).

3. Results

3.1. Supervised field trial

Chlorpyrifos and TCP residues in vegetables of supervised field trials are given in Table 1. The highest chlorpyrifos residue in raw vegetable sample was detected in spinach

Table 1
Chlorpyrifos and TCP residues (mg kg^{-1}) in fresh and processed vegetables of supervised field trial

Vegetables	MRL ^a	Processing	Total chlorpyrifos (Mean \pm SD)	Total TCP (Mean \pm SD)
Spinach (<i>n</i> = 5)	2.0	Raw	1.87 \pm 0.123	0.11 \pm 0.003
		Washed	1.25 \pm 0.115	0.10 \pm 0.004
		Peeled	NA	NA
		Cooked	0.771 \pm 0.019	0.21 \pm 0.007
Cauliflower (<i>n</i> = 5)	0.05	Raw	0.036 \pm 0.003	0.005 \pm 0.0001
		Washed	0.027 \pm 0.003	0.005 \pm 0.0001
		Peeled	NA	NA
		Cooked	0.019 \pm 0.002	0.017 \pm 0.002
Potato (<i>n</i> = 5)	0.2	Raw	0.136 \pm 0.015	0.009 \pm 0.0003
		Washed	0.095 \pm 0.007	0.008 \pm 0.0004
		Peeled	0.014 \pm 0.001	<LOQ
		Cooked	0.011 \pm 0.001	0.008 \pm 0.0008
Eggplant (<i>n</i> = 5)	1.0	Raw	1.25 \pm 0.125	0.015 \pm 0.005
		Washed	1.06 \pm 0.087	0.015 \pm 0.007
		Peeled	0.265 \pm 0.023	<LOQ
		Cooked	0.233 \pm 0.019	0.01 \pm 0.004
Tomato (<i>n</i> = 5)	0.5	Raw	0.420 \pm 0.029	0.006 \pm 0.0005
		Washed	0.378 \pm 0.025	0.006 \pm 0.0009
		Peeled	NA	NA
		Cooked	0.283 \pm 0.021	0.017 \pm 0.008
Okra (<i>n</i> = 5)	1.5	Raw	1.41 \pm 0.148	0.008 \pm 0.0009
		Washed	1.09 \pm 0.089	0.007 \pm 0.0005
		Peeled	NA	NA
		Cooked	0.813 \pm 0.025	0.012 \pm 0.006

NA means peeling was not done.

LOQ means limit of quantitation.

^a Maximum residue limit established by FAO/WHO (2004).

(1.87 mg kg^{-1}) followed by okra (1.41 mg kg^{-1}) and eggplant (1.25 mg kg^{-1}). The residue of chlorpyrifos was observed to be the lowest in cauliflower 0.036 (mg kg^{-1}). Similar trend of chlorpyrifos residue was found in the same samples after washing. The retention of chlorpyrifos residue after cooking in okra, spinach, tomato, eggplant, cauliflower and potato was 0.813, 0.771, 0.283, 0.233, 0.019 and 0.011 mg kg^{-1} , respectively.

The reduction of chlorpyrifos residue after washing, peeling and cooking is presented in Fig. 2. The effect of washing was found to be the most pronounced on spinach sample followed by potato and cauliflower but least effect was found on tomato samples. The process of washing decreased chlorpyrifos residue up to 33% in spinach, 30% in potato, 25% in cauliflower and 10% in tomato. Peeling decreased chlorpyrifos residue by 75% and 85% in eggplant and potato, respectively. The effect of cooking was found to be the most pronounced on spinach sample followed by cauliflower and okra but least effect was found on eggplant samples. The process of cooking decreased chlorpyrifos residue up to 38% in spinach, 29% in cauliflower and 25% in okra. The least effect of cooking was found in the case of eggplant in which the chlorpyrifos residue declined only by 12%.

3.2. Farmers field

The results of chlorpyrifos residue detected in vegetable samples collected from the farmer's field are presented in Table 2. The results indicated that at raw stage the highest chlorpyrifos residue was found in okra (0.021–1.930 mg kg^{-1}) followed by spinach (0.232–1.87 mg kg^{-1}) and eggplant (0.040–0.850 mg kg^{-1}). The residues were relatively low in cauliflower samples (0.017–0.063 mg kg^{-1}). At raw stage, the highest mean TCP residue was found in spinach (0.009 mg kg^{-1}); whereas, it was not detected in cauliflower and potato samples.

The findings revealed that the chlorpyrifos residue decreased due to washing of the vegetable samples but the trend remained identical to that of the raw stage. However, after cooking the retention trend of chlorpyrifos residue was changed. The spinach samples exhibited the highest mean residue (0.525 mg kg^{-1}) followed by okra (0.287 mg kg^{-1}) and eggplant (0.043 mg kg^{-1}). The chlorpyrifos residue was found to be the lowest in cauliflower (0.021 mg kg^{-1}) after cooking. The TCP concentration was not much affected by washing and amount remained almost the same as that of raw stage.

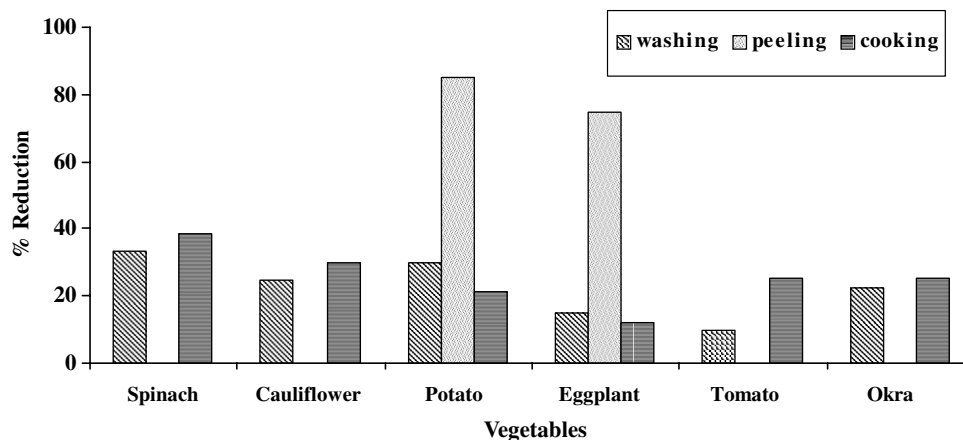


Fig. 2. Percent reduction of chlorpyrifos residues in vegetables of supervised field.

Table 2
Chlorpyrifos and TCP residues (mg kg⁻¹) in fresh and processed vegetables of farmers field

Vegetables	Processing	Total chlorpyrifos		Total TCP	
		Range	Mean ± SD	Range	Mean ± SD
Spinach (<i>n</i> = 40)	Raw	0.232–1.87	1.04 ± 0.515	ND–0.013	0.009 ± 0.0008
	Washed	0.206–1.57	0.825 ± 0.429	ND–0.012	0.008 ± 0.0007
	Peeled	NA	NA	NA	NA
	Cooked	0.077–1.21	0.525 ± 0.371	ND–0.120	0.023 ± 0.001
Cauliflower (<i>n</i> = 44)	Raw	0.017–0.063	0.033 ± 0.018	ND	ND
	Washed	0.014–0.043	0.024 ± 0.013	ND	ND
	Peeled	NA	NA	NA	NA
	Cooked	ND–0.035	0.021 ± 0.008	ND–0.007	0.004 ± 0.0008
Potato (<i>n</i> = 40)	Raw	0.026–0.241	0.104 ± 0.065	ND	ND
	Washed	0.019–0.181	0.079 ± 0.048	ND	ND
	Peeled	ND–0.042	0.027 ± 0.009	ND	ND
	Cooked	ND–0.02	0.014 ± 0.004	ND–0.007	0.003 ± 0.0006
Eggplant (<i>n</i> = 48)	Raw	0.040–0.850	0.453 ± 0.264	ND–0.010	0.005 ± 0.0009
	Washed	0.029–0.75	0.371 ± 0.220	ND–0.008	0.002 ± 0.0007
	Peeled	0.006–0.114	0.054 ± 0.031	ND	ND
	Cooked	0.005–0.081	0.043 ± 0.025	ND–0.04	0.017 ± 0.005
Tomato (<i>n</i> = 45)	Raw	0.065–0.435	0.214 ± 0.124	ND–0.01	0.004 ± 0.0009
	Washed	0.068–0.332	0.160 ± 0.095	ND–0.01	0.001 ± 0.0008
	Peeled	NA	NA	NA	NA
	Cooked	0.049–0.234	0.114 ± 0.07	ND–0.06	0.025 ± 0.003
Okra (<i>n</i> = 50)	Raw	0.021–1.930	0.529 ± 0.502	ND–0.018	0.006 ± 0.0008
	Washed	0.017–1.550	0.414 ± 0.400	ND–0.011	0.003 ± 0.0005
	Peeled	NA	NA	NA	NA
	Cooked	0.011–0.933	0.287 ± 0.255	ND–0.008	0.028 ± 0.004

NA means peeling was not done.

ND means not detected.

The data indicated that washing, peeling and cooking have significant effect on the declining of chlorpyrifos residue in different vegetables. The percent reduction of chlorpyrifos residue after washing was most prominent on cauliflower followed by tomato and potato but it had a least effect on eggplant (Fig. 3). The process of washing decreased chlorpyrifos residue by 27% in cauliflower, 25% in tomato, 24% in potato and 18% in eggplant. The act of peeling decreased chlorpyrifos residue by 65% and

85% in potato and eggplant, respectively. TCP residues were not detected in any of the peeled vegetable. The effect of cooking was higher on potato followed by spinach and okra. The chlorpyrifos residue decreased by 59.56% in potato and 48.10% in spinach. The least effect of cooking was found in the case of cauliflower and eggplant by 12% and 28%, respectively. TCP concentration was substantially increased in almost all of the vegetables by the act of cooking (Table 2).

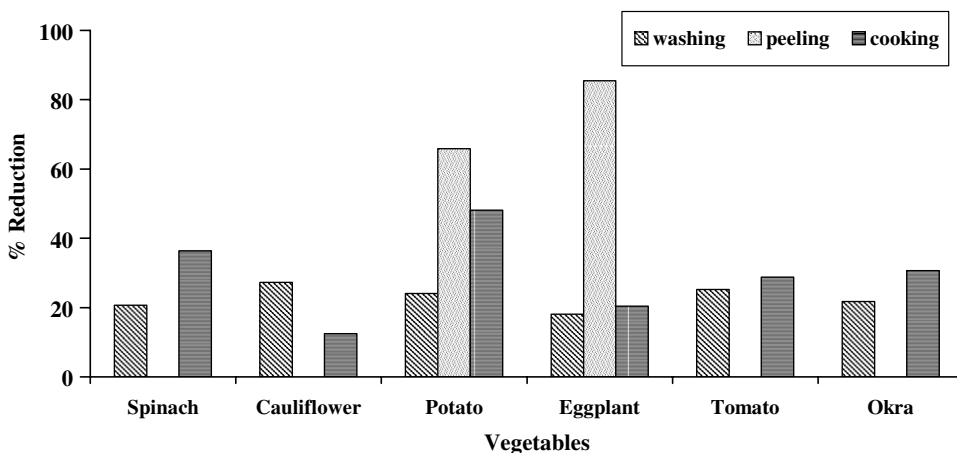


Fig. 3. Percent reduction of chlorpyrifos residues in vegetables of farmer's field.

Table 3
Summary of chlorpyrifos residues detected in farmer samples and number of samples at various concentrations at raw stage and after processing

Vegetables	MRL ^a	Processing	Concentration (mg kg ⁻¹) ^b									Total found	Number of violations
			ND ^c	<0.05	<0.1	<0.2	<0.5	<1	<1.5	<2	>2		
Spinach (<i>n</i> = 40)	2	Raw	4	0	0	0	8	8	12	8	0	36	0
		Washed	4	0	0	0	8	16	12	0	0	36	0
		Cooked	4	0	4	8	8	12	4	0	0	36	0
Cauliflower (<i>n</i> = 44)	0.05	Raw	4	32	8	0	0	0	0	0	0	40	8
		Washed	4	40	0	0	0	0	0	0	0	40	0
		Cooked	4	40	0	0	0	0	0	0	0	40	0
Potato (<i>n</i> = 40)	0.2	Raw	8	8	8	12	4	0	0	0	0	32	4
		Washed	8	12	4	16	0	0	0	0	0	32	0
		Peeled	12	28	0	0	0	0	0	0	0	28	0
		Cooked	8	24	4	4	0	0	0	0	0	32	0
Eggplant (<i>n</i> = 48)	1	Raw	4	4	4	4	8	24	0	0	0	44	0
		Washed	4	4	4	8	12	16	0	0	0	44	0
		Peeled	4	16	24	4	0	0	0	0	0	44	0
		Cooked	4	12	4	16	12	0	0	0	0	44	0
Tomato (<i>n</i> = 45)	0.5	Raw	12	0	8	9	16	0	0	0	0	33	0
		Washed	12	0	13	8	12	0	0	0	0	33	0
		Cooked	13	4	16	4	8	0	0	0	0	32	0
Okra (<i>n</i> = 50)	1.5	Raw	8	4	4	6	12	12	0	4	0	40	4
		Washed	8	8	2	4	16	8	4	0	0	42	0
		Cooked	10	8	4	8	16	4	0	0	0	40	0

^a Maximum residue limit established by FAO/WHO (2004).

^b Each column represents the number of the residues detected at a concentration greater than that of the previous column but less than the concentration of the column under consideration.

^c Not detected.

The vegetable samples collected from farmer's field further delineated that at raw stage 225 out of 267 samples contained detectable residues representing 84% rate of contamination. Except potato, cauliflower and okra, all the samples contained chlorpyrifos residue below the MRLs. In case of potato 4 out of 40, in cauliflower 8 out of 44 and in okra 4 out of 50 samples exceeded MRLs at raw stage (Table 3). But residue level of chlorpyrifos reduced below MRLs after washing and peeling. Cooking further lowered the residue in all of the vegetables (Table 3).

4. Discussion

In supervised field trial of vegetables, all the vegetables except eggplant were below the MRLs established by FAO/WHO (2004). The vegetables are short duration crops and in subtropical climate prevailing during growth and maturity of vegetables, it is necessary to spray the crops repeatedly during the entire period of growth and sometimes even at the fruiting stage (Kumari, Madan, Singh, Singh, & Kathpal, 2004). Chlorpyrifos is stable and fairly persistent being a member of the organophosphate pesticides (Chattopadhyay, 1993).

In vegetable samples collected from farmer's field, higher chlorpyrifos residue, exceeding MRL values was observed. The farmers are mostly illiterate about the safe and judicious use of pesticides. Farmers have a tendency to over-dose the pesticides to ensure a high external quality

of the produce (Dejonckheere, Steurbaut, Drieghe, Verstraeten, & Braeckman, 1996; Yen, Bekele, & Kalloo, 1999) and residue level of any pesticide in vegetable is primarily dependent on the application rate of the active ingredient (Sadlo, 2000). In addition, the repeated use of the pesticide in the field, particularly closer to harvest significantly contributes toward higher residues (Dogheim, Alla, El-Syes, Almazm, & Salama, 1996). The results of the present study accord with Dejonckheere et al. (1996), who reported that 24% of vegetable samples collected from farmers, were exceeding the MRL.

4.1. Effect of household processing on field incurred residues in vegetables

4.1.1. Effect of washing

A significant reduction (10–33%) in chlorpyrifos residue was observed during washing of the vegetables; whereas, the amount of TCP remained essentially the same as that of raw stage. Washing of produce has been shown to reduce the levels of chlorpyrifos residues that can be dissolved or physically dislodged from the raw agricultural commodity. In a previous study, OP residues were reduced by 9–40% on washing tomatoes and peppers, depending upon the type of crop and pesticide (Celik, Kunc, & Asan, 1995). Although water solubility of pesticide is an important factor during washing operation, yet it has not been reported by various researchers (Cabras et al., 1998; Walter

et al., 2000) and they concluded that water solubility of pesticide is not an important parameter in removal of pesticide residues from food crops. In the present study also, water solubility was not found to be the important factor during washing operation and the results from the current study are consistent with an earlier study which showed that residues of six pesticides on olives decreased after washing with no correlation to water solubility of the pesticides (Cabras, Angioni, Garau, Melis, & Pirisi, 1997). The results are also in line with some recent findings, where washing decreased chlorpyrifos, cypermethrin and ethylenebisdithiocarbamates residues in asparagus by 24%, 35% and 52%, respectively (Chavarri, Herrera, & Arino, 2005).

4.1.2. Effect of peeling

Eggplant and potato vegetables are eaten normally without their peel. Chlorpyrifos is a non-systemic insecticide. Results from the flesh after peeling indicated that chlorpyrifos residues practically remain in the peel, as only small amounts were identified in the flesh (Table 2). The data clearly indicate that peeling process had a significant effect on the removal of chlorpyrifos residue in eggplant and potato because of lower penetration power of the compound, incorporation into the cuticle layer of the plant surface and resulting in deposits removable by peeling (Dejonckheere et al., 1996). So, when peel was removed, greater amount of pesticide residue was removed. The presence of pesticide residues in skin of the tested vegetables indicates that peeling process is necessary to remove the pesticide residues from the commodity. These results are consistent with those reported in previous studies in potatoes with the non-systemic phenylcarbamate insecticide chlorpropham in potatoes, where the amount of residue removed by peeling was >90% (Lentza-Rizos & Balokas, 2001). Similar results were observed with the non-systemic organophosphate insecticides diazinon and parathion and the non-systemic pyrethroid insecticide cypermethrin in carrots, where the residue present in whole carrot were not detected after peeling (Burchat et al., 1998). These results closely relate with recent findings of Chavarri et al. (2005) who found 73% reduction in chlorpyrifos residues in asparagus after peeling.

4.1.3. Effect of cooking

The heat treatment during cooking exhibited a significant effect on decomposition of the chlorpyrifos in all the tested vegetable samples. The decrease ranged from 12% to 48%. The effect was more obvious in spinach (38%) followed by cauliflower (29%). However, complete removal of the chlorpyrifos was not observed in any of the vegetable. Similar results were stated by Wen, Shimamoto, Nishihara, and Kond (1985), who determined the stability of the toxic residues after the tubers were cooked in boiling water. They reported that use of such procedures removed higher percentages of pesticides. The results are consistent with a recent study, where frying reduced OP residues ranging

from 49% to 53% in potatoes (Soliman, 2001). In another study, 18% reduction in fenitrothion residues in kaki fruit was observed after boiling in water (Fernandez-Cruz, Villarroya, Llanos, Alonso-Prados, & Garcia-Baudian, 2004).

The concentration of TCP was substantially increased during the course of cooking and chlorpyrifos residue reduced in all the vegetables. This indicates breakdown of chlorpyrifos to TCP during cooking. The results suggested that some of the chlorpyrifos was lost by volatilization and some was degraded to TCP during heat treatment. Rates of degradation and volatilization of residues are increased by heat involved in the process. Byrne and Pinkerton (2004) reported that during canning of green beans, the chlorpyrifos concentrations decreased from an average of 2328 to an average of 832 ng g⁻¹, while TCP concentrations increased from an average of 56 to 159 ng g⁻¹. The results are also in proximity with a recent study where fenitrothion residue was decreased during cooking in boiled whole kaki and the concentration of its metabolite 3-methyl-4-nitrophenol increased after boiling from 0.080 to 0.093 mg kg⁻¹ (Fernandez-Cruz et al., 2004).

5. Conclusion

From the above results, it is clear that the advantages of the application of pesticides in agriculture in producing better crops must be weighed against the possible health hazard arising from the toxic pesticide residues in food. Pesticides should be applied correctly according to good agricultural practices, using only the required amounts. Although higher residue of chlorpyrifos was observed in some vegetables collected from farmers field but their levels dropped to below MRL values by food processing. Washing with water is also necessary to decrease the intake of pesticide residues. Cooking of vegetables helps to eliminate most of the pesticide residues. Further studies on the degradative behavior of chlorpyrifos during thermal processing are needed.

References

- Anonymous (2000). Office of Prevention, Pesticides and Toxic Substance Chlorpyrifos; *Revised Product and Residue Chemistry Chapters*; US Environmental Protection Agency Washington, DC, June 20.
- Athanasopoulos, P. A., & Pappas, C. (2000). Effects of fruit acidity and storage conditions on the rate of degradation of azinphos methyl on apples and lemons. *Food Chemistry*, 69, 69–72.
- Burchat, C. S., Ripley, B. D., Leishman, P. D., Ritcey, G. M., Kakuda, Y., & Stephenson, G. R. (1998). The distribution of nine pesticides between the juice and pulp of carrots and tomatoes after home processing. *Food Additives and Contaminants*, 15, 61–71.
- Byrne, S. L., & Pinkerton, S. L. (2004). The effect of cooking on chlorpyrifos and 3,5,6 trichloro-2-pyridinol levels in chlorpyrifos-fortified produce for use in refining dietary exposure. *Journal of Agricultural and Food Chemistry*, 52, 7567–7573.
- Cabras, P., & Angioni, A. (2000). Pesticide residues in grapes, wine, and their processing products. *Journal of Agricultural and Food Chemistry*, 48, 967–973.

- Cabras, P., Angioni, A., Garau, V. L., Melis, M., Pirisi, F. M., et al. (1997). Residues of some pesticides in fresh and dried apricots. *Journal of Agricultural and Food Chemistry*, *45*, 3221–3222.
- Cabras, P., Angioni, A., Garau, V. L., Minelli, E. V., Cabitza, F., & Cubeddu, M. (1998). Pesticide residues in prune processing. *Journal of Agricultural and Food Chemistry*, *46*, 3772–3774.
- Celik, S., Kunc, S., & Asan, T. (1995). Degradation of some pesticides in the field and effect of processing. *Analyst*, *120*, 1739–1743.
- Chattopadhyay, S. B. (1993). *Principles and procedures of plant protection* (3rd ed.). New Delhi: Oxford and IBH Publishing Co. Pvt. Ltd., pp. 99.
- Chavarri, M. J., Herrera, A., & Arino, A. (2005). The decrease in pesticides in fruits and vegetables during commercial processing. *International Journal of Food Science and Technology*, *40*, 205–211.
- Chin, H. B. (1991). The effect of processing on residues in foods: The food processing industry's database. In B. G. Tweedy (Ed.), *Pesticide residues and food safety: A harvest of view-points* (pp. 175–181). Washington, DC: American Chemical Society.
- Dejonckheere, W., Steurbaut, W., Drieghe, S., Verstraeten, R., & Braeckman, H. (1996). Pesticide residue concentrations in the Belgian total diet, 1991–1993. *Journal of AOAC International*, *79*, 520–528.
- Dogheim, S. M., Alla, S. A. G., El-Syes, S. M. A., Almazm, M. M., & Salama, E. Y. (1996). Organochlorine and organophosphorus pesticide residues in food from Egyptian local markets. *Journal of AOAC International*, *79*, 949–952.
- Elkins, E. R. (1989). Effect of commercial processing on pesticide residues on selected fruits and vegetables. *Journal of AOAC International*, *72*, 533–535.
- FAO/WHO, (2004). Codex Alimentarius Commission. <http://apps.fao.org>.
- Fernaandez-Cruz, M. L., Villarroja, M., Llanos, S., Alonso-Prados, J. L., & Garciaa-Baudian, J. M. (2004). Field-incurred fenitrothion residues in kakis: Comparison of individual fruits, composite samples, and peeled and cooked fruits. *Journal of Agricultural and Food Chemistry*, *52*, 860–863.
- Kadenezki, L., Arpad, Z., Gardi, I., Ambrus, A., Gyorfi, L., Reese, G., et al. (1992). Column extraction of residues of several pesticides from fruits and vegetables; a simple multiresidue analysis method. *Journal of AOAC International*, *75*, 53–61.
- Kilgore, L., & Windham, F. (1970). Disappearance of malathion residue in broccoli during cooking and freezing. *Journal of Agricultural and Food Chemistry*, *18*, 162–163.
- Kumari, B., Madan, V. K., Singh, J., Singh, S., & Kathpal, T. S. (2004). Monitoring of pesticidal contamination of farmgate vegetables from Hisar. *Environmental Monitoring and Assessment*, *90*, 65–71.
- Lentza-Rizos, C. H., & Balokas, A. (2001). Residue levels of chlorpropham in individual tubers and composite samples of postharvest-treated potatoes. *Journal of Agricultural and Food Chemistry*, *49*, 710–714.
- Mahindru, S. N. (2004). Health and environmental effects of pesticides. In *Food contaminants: Origin, propagation and analysis* (pp. 41). New Delhi: APH Publishing Corporation.
- Oliver, G. R., Bolles, H. G., & Shurdut, B. A. (2000). Chlorpyrifos: Probabilistic assessment of exposure and risk. *Neurotoxicology*, *21*, 203–208.
- Sadlo, S. (2000). Quantitative relationship of application rate and pesticide residues in green house tomatoes. *Journal of AOAC International*, *83*, 214–219.
- Soliman, K. M. (2001). Changes in concentrations of pesticide residues in potatoes during washing and home preparation. *Food and Chemical Toxicology*, *39*, 887–891.
- Walter, J. K., Arsenault, T. L., Pylypiw, H. M., & Mattina, M. J. I. (2000). Reduction of pesticide residues on produce by rinsing. *Journal of Agricultural and Food Chemistry*, *48*, 4666–4670.
- Wen, K. C., Shimamoto, T., Nishihara, T., & Kond, M. (1985). Behavior of pesticides during cooking treatments in food samples. *Journal of Hygienic Chemistry*, *13*, 256–259.
- Yen, I. C., Bekele, I., & Kallou, C. (1999). Use patterns and residue levels of organophosphate pesticides on vegetables in Trinidad, West Indies. *Journal of AOAC International*, *82*, 991–995.