

Processing Factors and Removal Ratios of Select Pesticides in Hot Pepper Leaves by a Successive Process of Washing, Blanching, and Drying

Mi-Gyung Lee* and Da-i Jung

Food Science & Biotechnology Division, Andong National University, Andong, Gyeongbuk 760-749, Korea

Abstract Six pesticides were determined in hot pepper leaves after successive processing steps of washing, blanching, and drying. The tested pesticides included dichlofluanid, flusilazole, folpet, iprodione, λ -cyhalothrin, and lufenuron. Each pesticide was singly applied to the leaves of the pepper plants, which were being cultivated in a greenhouse. The processing factors were dependent on the type of pesticide, and were in the following ranges: 0.09-0.73 by washing, <0.00-0.48 after blanching, and <0.00-3.30 after drying. Only lufenuron showed a processing factor of more than 1, at 3.30 in dried leaves, while the processing factors of the other pesticides were less than 1. The removal ratios of the tested pesticides by washing ranged from 27 to 90%. The blanching step increased their removals by 10-25%. However, drying did not have an effect on residue reduction. Finally, after proceeding to the drying step, removal ratios ranged from 85 to 100%, with the exception of lufenuron at 47%.

Keywords: pesticide, processing factor, removal ratio, hot pepper leaf, residue reduction

Introduction

The leaves of hot peppers (Capsicum annuum var. annuum L.) as well as their fruits are deemed edible in Korea. Like other leafy vegetables, Koreans enjoy pepper leaves as namul, a dish prepared by mixing the leaves with several seasonings. Farmers or market distributors typically sell pepper leaves after washing, blanching, and drying. Thus, consumers can purchase such dried leaves through local markets.

Regarding the safety assurance of pepper leaves, pesticide residues may be of concern since high levels have been detected (1,2). Pepper leaves are often an additional harvest acquired along with the immature green peppers grown in greenhouses or the mature red peppers grown in fields. When a regulatory agency approves use of pesticide on hot pepper, it should need to consider both the fruit and the leaves, which are differentiated in terms of their residue magnitudes and dietary importance. Green pepper fruits are harvested many times during greenhouse cultivation, and this leads to fewer pesticide applications and lower amounts of residue. On the other hand, the leaves are picked once at the end of the final fruit harvest, which results in exposure to an increased number of pesticide applications and much higher amounts of residue on the leaves. One report providing field residue data for 52 kinds of pesticides showed that, on average, the maximum residue level in pepper leaves was as high as 29 times that in the fruit (3).

Pesticide applications are unavoidable to protect pepper plants from viral diseases, phytophthora blight, anthracnose, helicoverpa assulta, etc (4). Lee *et al.* (5) reported through

*Corresponding author: Tel: +82-54-820-6011; Fax: +82-54-820-6264 E-mail: leemig@andong.ac.kr Received December 15,2008; Revised May 21, 2009; Accepted May 24, 2009 a pesticide usage survey that the average number of pesticide applications was 10 times per greenhouse farm. And 7 kinds of pesticides were used per farm at levels totaling 0.01-5.00 kg active ingredient (a.i.)/ha. Presently, the Rural Development Agency of Korea requires that the pesticide industry include a phrase such as "prohibition of distribution or sale of pepper leaves for food" on labels for specified pesticides.

For the most part, pesticide residues in food commodities are reduced or concentrated after cooking or processing. The change in the amount of residue is expressed as a processing factor or transfer factor. Presently, most regulatory agencies consider processing factors when they approve new pesticides for use, as well as to set legal limits and assess dietary intakes of pesticides of interest (6).

Many researchers have performed studies to determine how much residue can be eliminated by washing, blanching, and drying (7-13). Regarding pepper leaves, there is limited information probably because their consumption is rare on a worldwide scale. As far as we know, Lee *et al.* (14) has been the only group to report on the removal effects of pesticides using naturally contaminated samples.

The aim of this study was to better understand the removal effects of different pesticide residues in processed pepper leaves, by performing washing, blanching, and drying steps. Further, it was to obtain processing factors to utilize in setting maximum residue limits for pepper leaves.

Materials and Methods

Application of pesticides and harvesting of pepper leaves The applied pesticide formulations were wettable powders of 50% active ingredient (a.i.) for dichlofluanid, folpet, and iprodione, and an emulsifiable concentrate of 50% a.i. for lufenuron. For λ -cyhalothrin and flusilazole, a wettable powder of 1% a.i. and a suspended concentrate of 1.5% a.i. were used, respectively. A spray solution of each

pesticide was prepared by diluting the pesticide formulation with water by a factor of 500, 1,000, or 2,000 times, following usage guidelines (15) or a twice higher concentration.

For each pesticide, 2 L of spray solution was applied to the leaves of 10 pepper plants that were being cultivated in a greenhouse using a hand sprayer. The pepper leaves were harvested on the 3rd day after 1 pesticide application. The harvested leaves were then subjected to a successive process of washing, blanching, and drying. The experiments were repeated in triplicate. The protocol was repeated at intervals of 2 or 3 weeks from early September to the end of October. However, for flusilazole only, triplicate replications were conducted on the same day in mid-September. One kg of pepper leaves was harvested and 200 g were used for each processing (Fig. 1).

Methods of washing, blanching, and drying The removal effects of the pesticides from the pepper leaves were assessed by washing, by blanching after washing, and by drying after washing and blanching (Fig. 1). These processing steps were performed as closely as possible to the actual practices. For washing, 200 g of fresh leaves were stirred 60 times by hand for 1 min in 10 L of water in a stainless vessel. After draining the leaves using a sieve, they were washed again in the same manner. Again after draining, the leaves were left at a room temperature momentarily. Their measured weight was 205.5 g.

Blanching was performed using the washed leaves, which were cooked for 1 min with 6 L of boiling water in a lidded vessel. After heat treatment, the leaves were drained using a sieve and squeezed by both hands to remove the water. The weight of the blanched sample was 215.5 g.

For drying, the blanched leaves were spread on a plate covered with aluminum foil and dried in a hot air-dryer at 55°C for 3-4 hr, per the usual practice at farms. Also, the leaves were turned to ensure complete drying. The weight of the dried leaves was 33.2 g.

Analyses of pesticides The pesticide standards were purchased from Sigma-Aldrich (St. Louis, MO, USA) or Chem Service (West Chester, PA, USA). The employed organic solvents and sodium sulfate were residue-analysis

grade (Kanto Chemical, Tokyo, Japan). Florisil (60-100 mesh; Sigma-Aldrich) was activated for 4 hr at 130°C before using. All other reagents were of reagent grade. A homogenizer (Polytron; Kinematica Inc., Lucerne, Switzerland) and a rotary evaporator (Büchi, Flawil, Switzerland) were used to macerate and concentrate the samples, respectively. To determine the pesticide residues, a gas chromatograph (GC, 6890 Plus; Agilent Technologies, Santa Clara, CA, USA) equipped with an electron capture detector (ECD) or a nitrogen phosphorus detector (NPD) was used. The column was an HP-5 (30 m \times 0.32 mm \times 0.25 μ m; Agilent Technologies).

An analytical method for each pesticide was developed based primarily on the Official Analytical Methods of Pesticides (16), as described below. Twenty g of fresh leaves, or an equivalent amount to that for the washed and blanched samples, were subjected to pesticide analysis. For the dried leaves, analysis was conducted after soaking the leaves for 1 hr in 20 mL of water.

Dichlofluanid: The analytical method for dichlofluanid was developed by modifying the clean-up step of Analysis Methods No. 10, 58, and 83 (16). Acetone was used to extract residue from the samples. From 150 mL of extract, a 30 mL aliquot was diluted with 10 mL of saturated NaCl solution and 100 mL of water, and then partitioned twice with 25 mL of dichloromethane (DCM). The combined DCM layers were dehydrated with sodium sulfate prior to concentrating to dryness in a rotary evaporator. Then, the sample was dissolved in 5 mL of *n*-hexane. For clean-up, 5 g of florisil was used as the adsorbent. The first eluate using 50 mL of DCM: *n*-hexane (50:50, v/v) was discarded and the next eluate using 50 mL of DCM:acetonitrile:nhexane (50:0.35:49.65, v/v/v) was retained. The sample was evaporated to dryness, resolved with n-hexane, and subjected to gas chromatography (GC). The GC operating conditions were as follows: the NPD detector was set at 280°C, the temperature of the injector was 260°C, and the injected amount of sample was 1 µL in the splitless mode. Nitrogen was used as the carrier gas at 1.0 mL/min. The column temperature was controlled as follows: 2 min at 80°C, and then rising by 10°C/min to 280°C and holding for 10 min.

Flusilazole: This analysis employed modifications to Methods No. 5, 58, and 83 (16) as follows. A 150 mL

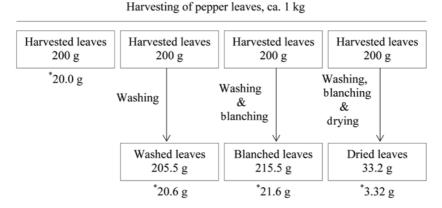


Fig. 1. Processing procedures of pepper leaves and sample amounts for pesticide analysis. *Sample amount taken for pesticide analysis.

1078 M. -G. Lee and D. -I Jung

amount of acetone extract was concentrated in a rotary evaporator. The concentrate was mixed with 50 mL of saturated NaCl solution and 50 mL of water, partitioned with 100 mL of *n*-hexane, and then again with 50 mL *n*hexane. The combined extract was dehydrated with sodium sulfate and concentrated up to 5 mL. Next, 8 g of florisil and *n*-hexane: acetone (85:15, v/v) were used to clean-up the residue. The first eluted 40 mL was discarded and the consecutively received 120 mL was retained. After evaporating the sample to dryness, it was dissolved with 5 mL of acetone. The conditions for GC were as follows. The NPD detector was set at 280°C. The column temperature of the HP-5 was held at 100°C for 3 min, and then increased by 10°C/min to 280°C and held for 2 min. A 2 μL amount of sample was injected in the splitless mode. Nitrogen was used as the carrier gas at 1.0 mL/min.

Folpet: To analyze folpet, modifications to Methods No. 2, 58, and 83 (16) were used. The main modification was sample acidification to prevent the breakdown of folpet residue during maceration of the leaves. In addition, there were changes in the eluting solvents for the clean-up step. Before homogenizing the pepper leaves, 2 mL of 2 N HCl were added to the sample. From 200 mL of the sample extracted using acetonitrile, an aliquot of 100 mL was partitioned with 50 mL of petroleum ether:DCM (80:20, v/v). The organic layer was washed twice with 5 mL of saturated NaCl solution and 100 mL of water. It was then dehydrated with sodium sulfate and concentrated in a rotary evaporator. The sample was loaded into a glass column packed with 20 g of florisil and was washed-up with 200 mL of petroleum ether:DCM (80:20, v/v). Next, the mixed solvent of petroleum ether:DCM:acetonitrile (70:30:1.5, v/v/v) was loaded onto the column. The first eluted 60 mL was discarded and the next 70 mL was collected. After evaporating the sample to dryness, it was resolved with 10 mL of benzene. For GC, an ECD was used and 1 µL of sample was injected in the split mode, 50:1. The other GC conditions were the same as those for dichlofluanid.

Iprodione: Modifications to Analysis Methods No. 58 and 83 were employed, with a particular change in the eluting solvents during clean-up using florisil. The acetone extraction and partitioning with DCM were performed in the same manner as for dichlofluanid. For clean-up, 5 g of florisil was used as the adsorbent. A 50 mL amount of DCM:acetonitrile:*n*-hexane (50:1:49, v/v/v) was passed through a column and discarded. Then, 50 mL of DCM: acetonitrile:*n*-hexane (50:3:49, v/v/v) was loaded onto the column and the eluate was retained. It was then evaporated to dryness and resolved with 5 mL of *n*-hexane. For GC see the method for folpet.

λ-Cyhalothrin: Modifications to Analysis Methods No. 6 and 83 (16) were used. From 200 mL of sample extracted with acetone, a 40 mL aliquot was concentrated to dryness in a rotary evaporator. Next, a coagulating process was performed. Here, 50 mL of coagulating solution, 2 g of Celite 545, and 5 mL of acetone were added to the sample and allowed to stand for 2 min. The mixture was then filtered through a glass filter (17G3; YoungJin Co., Seoul, Korea). The coagulating solution was prepared by a 10-fold dilution of the original coagulation solution, which included 2 g of NH₄Cl, 4 mL of H₃PO₄, and 400 mL of

water. The obtained filtrate was partitioned twice using 50 mL of DCM. The organic layer was dehydrated, concentrated, and dissolved with 10 mL of *n*-hexane. The sample was loaded onto a florisil Sep-Pak cartridge (900 mg; Waters, Milford, MA, USA) and consecutively 20 mL of *n*-hexane:ethyl ether (5:5, v/v) was passed through. The eluate was retained, evaporated to dryness, and resolved with 5 mL of *n*-hexane. For GC see the method for iprodione.

Lufenuron: Analysis Method No. 83 (16) was employed with substantial changes. Specifically, CN and silica Sep-Pak cartridges were used for clean-up. A 100 mL aliquot of 200 mL of sample extracted with methanol was partitioned with 30 mL of saturated NaCl solution, 20 mL of water, and 100 mL of *n*-hexane:diethylether (9:1, v/v). The sample was then partitioned again by adding 50 mL of n-hexane:diethylether (9:1, v/v). The combined organic layers were taken and dehydrated. The sample was evaporated to dryness and dissolved with 2 mL of nhexane. Next, it was loaded onto a CN cartridge (500 mg; Supelco, Bellefonte, PA, USA), and *n*-hexane:diethylether (1:1, v/v) was passed through the cartridge. The first eluted 2 mL was discarded and the next 8 mL was taken. The sample was then concentrated to dryness and dissolved with 2 mL of *n*-hexane. Finally, the sample was subjected to a silica Sep-Pak cartridge (500 mg; Waters) and nhexane:diethylether (1:1, v/v) was passed through. The eluted 7 mL was taken, evaporated to dryness, resolved with 4 mL of *n*-hexane:methanol:isopropanol (90:5:5, v/v/vv), and used for GC. For the GC conditions see the method for folpet.

The recovery of each pesticide was tested using untreated pepper leaves fortified at levels of 0.5-2.0 mg/kg. The determined limits of quantification (LOQ), measured at a signal to noise ratio of more than 10 times, were 0.02 mg/kg for flusilazole and 0.1 mg/kg for the other pesticides.

Results and Discussion

Residue amounts in harvested leaves The recoveries for each pesticide in the pepper leaves ranged from 70 to 120%, with standard deviations (SDS) of less than approximately 10% (Table 1), which were deemed acceptable. These results offered proof for the appropriateness of the analytical methods used in this study.

The pepper leaves, grown in a greenhouse, were treated with pesticides, harvested, and processed. One pesticide application was performed, and the preharvest interval was 3 days.

The pesticide residue levels in the harvested leaves varied according to the kind of pesticide chemical applied (Table 2). Notably, the residue level for folpet was more than 100 mg/kg. Dichlofluanid and iprodione did not show such similarly high residue levels to folpet, even though their formulation types were the same as that of folpet (wettable powder containing 50% a.i.). Such a result for folpet cannot be explained by this study. However, we assume that it is resistant to photodegradation by sunlight. The photodegradation of pesticides is a key factor affecting residue amounts on crops (17). In addition, a high residue level may be due to an adjuvant included in the formulation,

Table 1. Pesticide recoveries by the analytical methods i	ısed in
this study	

	Added -	Recovery (n=3)					
Pesticide	concentration (mg/kg)	Mean	Relative standard deviation, %				
Dichlofluanid	1.5	120.0	8.5				
Flusilazole	0.5	95.4	2.1				
Folpet	1.5	70.0	10.5				
Iprodione	1.0	105.0	8.9				
λ-Cyhalothrin	1.0	95.9	7.4				
Lufenuron	1.5	72.0	9.4				

which is used to raise the adhesion of the pesticide to the plant. Cabras *et al.* (18) reported that folpet showed resistance to washing in grapes, which may have been attributed to an adjuvant included in the pesticide formulation, although the residue was found almost entirely on the surface of the grapes.

According to the experimental replicates, namely the 1st, 2nd, and 3rd pesticide applications, gradual increases in the residue levels appeared, except for flusilazole. This may have been due to a gradual decrease in sunlight during the experimental period, from September to October. There was no decrease in flusilazole because its replication was conducted on the same day.

Effects of washing All tested pesticides were removed by water washing by more than 70%: dichlofluanid, 84%; flusilazole, 76%; folpet, 90%; iprodione, 80%; λ-cyhalothrin, 70% (Table 2). The exception was lufenuron at 27%. The initial residue levels for folpet were as high as 133-186 mg/ kg; however, water washing removed the residue remarkably. Pesticide residue removal in foods by cooking or processing depends on the kind of pesticide and the type of food. One review paper demonstrated a wide range of removal ratios (0-97%) for different pesticides by washing different foods (7). The lesser removal of lufenuron may be due to its lipophilic property (log P=5.12, the log value of the octanol-water partition coefficient). This is supported by Lee et al. (14) who reported in a pepper leaf experiment that lipophilic pesticides such as α -cypermethrin, bifenthrin, and esfenvalerate (log P=5.5-6.4), belonging to the synthetic pyrethroid group, were only removed by 27-33% through water washing. Similar lower removal effects by washing have been demonstrated for synthetic pyrethroid pesticides in Chinese cabbage, as reported by Kang and Lee (8). Boulaid et al. (11) also reported small removals of lipophilic pesticides, including pyrifenox, pyridaben, and tralomethrine (log P=4-6) in the washing of tomatoes. Nevertheless, the results of the present study did not show a correlation between lipophilicity and pesticide removal in a regression analysis (y=7.156x+0.3032, R^2 =0.2).

Lufenuron is systemic in its mode of action on plants. A systemic pesticide can penetrate and translocate into a plant. While a non-systemic pesticide cannot penetrate into a plant, and forms deposits on the surfaces of leaves and fruits (18). Thus, a non-systemic pesticide deposited on the surface of a plant may be more effectively removed by

washing. In this study, λ -cyhalothrin was removed at a higher rate than lufenuron, even though λ -cyhalothrin is more lipophilic. Such a result may be due to differences in systemic and non-systemic properties, in which λ -cyhalothrin is non-systemic and lufenuron is systemic.

Also, Lee *et al.* (14) reported that imidacloprid, having high water solubility (log P=0.57), was not removed by washing pepper leaves as much as was expected, and such a result may be due to its systemic property. Recently, researchers such as Krol *et al.* (20), Christensen *et al.* (10), and Angioni *et al.* (21) have strongly supported such a view, suggesting that water solubility is not the important factor, but rather the systemic or non-systemic properties of the pesticide may be more important for its removal.

At the present time, it is not certain what pesticide properties are more related to removal by the water washing of foods. In this study, the removal of lufenuron was likely dependent on its two properties: lipophilic and systemic.

Effects of blanching and drying Most of the initial pesticide residues in the harvested leaves were removed after blanching [(Table 2); dichlofluanid (100%), folpet (100%), and λ -cyhalothrin (95%)]. The removal ratios of iprodione and flusilazole reached 85%. With respect to lufenuron, blanching removed an additional 20% of residue, and accordingly, a total of 47% was removed. Folpet, which had a high initial amount of residue, was removed satisfactorily. Thus, the blanching process was effective for removing pesticides in pepper leaves, and increased removal ratios by 5-25%. Lee et al. (14) also demonstrated the effectiveness of blanching, by reporting that the blanching of washed pepper leaves increased the removal ratios of 6 pesticides by 54-62%. Here, it needs to be noted that the blanching process included a squeezing step, to eliminate excess water after heating the leaves. Through squeezing, pesticide residue would likely be effectively leached from the pepper leaves.

During the blanching or cooking of vegetables, pesticides can be eliminated through mechanisms such as hydrolysis, volatilization, and leaching. Most of these phenomena arise in relation to the physicochemical properties of pesticide chemicals. The residue ratios for blanched spinach ranged from 6% for volatile dichlorvos to 100% for some pyrethroid compounds (8). In the case of cauliflower heat treated for 15 min, captan residues were degraded completely, whereas fenitrothion levels did not decrease significantly (22). In this study, there were some differences in removal effects according to the kinds of pesticides; however, they were not remarkable. It is possible that the washing process, conducted prior to blanching, shielded some of the removal effects of blanching.

The inclusion of drying did not remove any additional residue. And the pesticide residue remaining in the blanched leaves was completely retained in the dried leaves. Moreover, moisture losses increased residue concentrations. When comparing concentrations of dichlofluanid, folpet, and λ -cyhalothrin in the dried leaves with their initial concentrations in harvested leaves, their removal ratios were more than 95%. Flusilazole and iprodione had removal ratios of 85%, and the concentration levels between the two were similar. Even though considerable

1080 M. -G. Lee and D. -I Jung

Table 2. Changes in pesticide residue levels for pepper leaves by successive processing

Pesticide application & processing		Dichlofluanid		Flusilazole ¹⁾		Folpet		Iprdione		λ-Cyhalothrin		Lufenuron	
	Processing	Mean ²⁾ (mg/kg)	RSD (%)	Mean (mg/kg)	RSD (%)	Mean (mg/kg)	RSD (%)	Mean (mg/kg)	RSD (%)	Mean (mg/kg)	RSD (%)	Mean (mg/kg)	RSD (%)
1 st	After harvesting	7.153	0.8	3.223	2.4	132.819	2.9	4.856	9.2	0.296	9.1	5.940	0.3
	Washing	1.179	18.2	0.811	5.3	16.553	4.8	0.417	18.9	0.092	1.3	4.722	0.7
	Washing +Blanching	<0.1 ³⁾	0.0	0.367	21.3	0.020	10.0	0.608	5.9	<0.1	0.0	3.675	3.4
	Washing +Blanching +Hot air-drying	<0.1	0.0	3.107	0.6	0.047	10.0	4.192	8.9	<0.1	0.0	25.453	4.1
2 nd	After harvesting	27.621	10.3	2.431	3.5	170.214	2.3	6.159	4.1	0.810	13.1	6.392	2.7
	Washing	4.844	17.7	0.563	6.9	12.331	2.3	0.852	4.1	0.167	20.4	4.539	1.9
	Washing +Blanching	< 0.1	0.0	0.284	5.6	0.042	14.3	0.394	2.8	<0.1	0.0	2.767	2.0
	Washing +Blanching +Hot air-drying	<0.1	0.0	2.411	0.9	0.532	9.8	2.808	5.0	0.126	5.6	19.053	7.2
3 rd	After harvesting	77.763	11.0	2.805	4.2	185.515	2.3	7.397	15.4	0.948	8.5	6.348	4.0
	Washing	11.761	21.7	0.654	1.4	12.873	0.3	2.759	3.4	0.369	14.9	4.383	1.0
	Washing +Blanching	< 0.1	0.0	0.328	5.8	0.064	17.2	1.179	18.8	<0.1	0.0	2.558	5.0
	Washing +Blanching +Hot air-drying	<0.1	0.0	1.816	0.5	0.780	4.1	7.837	15.4	0.114	20.2	16.673	2.5
1 st+2 nd+3 rd	Washing	84 ⁴⁾	6 ⁵⁾	76	4	90	33	80	75	70	30	27	7
	Washing +Blanching	~100	0	85	0.3	99.9	0	85	42	95	78	47	25
	Washing +Blanching +Hot air-drying	~100	0	85	22	99.9	0	85	39	95	20	47	26

¹⁾For flusilzole, 1st, 2nd, and 3rd experiments were conducted on the same date; the other pesticides, on different dates between September to October.

amounts of these pesticides were eliminated, residue concentrations had increased due to moisture losses by drying. Also, lufenuron, which showed a much lower removal ratio of 47%, had a remarkable concentration increase in the dried leaves for the same reason of moisture loss.

In experiments of pepper leaves, Lee *et al.* (14) reported that the addition of a drying step increased residue reductions by 1-7%. In the current study, the blanched leaves were dried in a hot air oven at 55°C for 3-4 hr, while Lee *et al.* (14) dried their leaves in sunlight for 3 days. Such a difference in drying methods may be the cause of varied results. And sun-drying may improve residue reduction by photodegradation. Regarding hot air-drying, Chun and Lee (9) reported high removal effects for

pesticides in hot peppers. However, the hot peppers were dried under rigorous conditions, namely at 65°C for 26 hr. Even though there are reported data showing the effects of drying, these effects are very small as compared to washing or blanching. Thus, it may be considered that the removal effects by drying are negligible.

Processing factors and removal ratios Processing factors were calculated as the ratio of residue concentration in the processed leaves (mg/kg) to the residue concentration in the harvested leaves (mg/kg). If a processing factor is less than 1, it indicates the reduction of a pesticide, while if more than 1, it indicates a concentration in a regulatory practice, regardless of changes in volume or weight for the processed food. When a food sample has no change in

²⁾Pesticide concentrations in pepper leaves after processing were expressed as means (mg/kg); RSD, relative standard deviations (%) (n=3).

³⁾ <0.1 indicates that the detected pesticide was below the LOQ.

⁴⁾The 1st number of the bold values for each pesticide designates the mean value of the removal ratios (%) resulting from the 1st, 2nd, and 3rd experiments.

⁵⁾The 2nd value is the RSD of the mean removal ratio.

Mean \pm SD $(n=3)^{1)}$ Processing Dichlofluanid Flusilazole λ-Cyhalothrin Folpet Iprodione Lufenuron 0.16 ± 0.01 0.24 ± 0.01 0.09 ± 0.03 0.20 ± 0.15 0.30 ± 0.09 0.73 ± 0.05 Washing Washing <0.00±0.00 0.12 ± 0.01 0.00 ± 0.00 0.12 ± 0.05 $< 0.09 \pm 0.07$ 0.48±0.12 +Blanching Washing <0.00±0.00 0.87 ± 0.19 0.00 ± 0.00 0.79 ± 0.31 0.15 ± 0.03 +Blanching 3.30 ± 0.87 +Hot air-drying

Table 3. Processing factor for each pesticide after successive processing of pepper leaves

weight after processing, the processing factor rightly reflects the removal ratio of the pesticide. However, when there is a change resulting from drying, evaporating or concentrating, diluting, etc, the ratio removal should be calculated by considering the weight change.

In this study, we obtained processing factors by the following processing steps: washing; the combination of washing and blanching; and the combination of washing, blanching, and drying (Table 3). The processing factors by washing ranged from 0.09 to 0.73, depending on the kind of pesticide. And after washing and blanching, they ranged from <0.00 to 0.48. Washing or blanching only lead to slight changes in the sample weights (Fig. 1). Thus, the removal ratios for these processing steps are easily understandable as 27-90% by washing and 47-100% by washing and blanching.

For the drying process, the processing factors ranged from <0.00 to 3.30, depending on the kind of pesticide. Only lufenuron showed a factor of more than 1 at 3.30, and those of the other pesticides were less than 1. Thus, from a regulatory perspective, this is valuable information as lufenuron appears to concentrate in pepper leaves through washing, blanching, and drying. The reason why lufenuron had such a high processing factor can be explained as follows. First, lufenuron was removed less by washing due to its lipophilic and systemic properties. In addition, drying had no effect on its removal similarly to the other pesticides. Secondly, because the weight of the sample was reduced approximately 6 fold through drying, there was a corresponding increase in its residue level.

The variations in processing factors according to the experimental replications are expressed as means with standard deviations (Table 3). These ranged from 0 to 78%. Study data on processing factors indicate that variations can be caused by the application procedures for pesticides on plants, as well as the pesticide analysis and food processing. In a field residue study conducted in two stages of pesticide application and its analysis, minimum variations in results were from 30-40% (23). Reports by Boulaid *et al.* (11) and Christensen *et al.* (10) justify our results very well by showing similar data, in which maximum variations in processing factors were 67 and 74%, respectively.

In conclusion, we found that different types of pesticides remain in dried pepper leaves at very low concentrations after washing, blanching, and drying steps. Therefore, maximum residue limits should be set for pepper leaves by utilizing the processing factors obtained in this study. In addition, we suggest there is a need to determine pesticides that are resistant to removal under processing conditions, such as lufenuron.

Acknowledgments

This study was financially supported from the Korea Crop Protection Association and Andong National University (2006 Research Fund).

References

- Jeon JS, Kwon MJ, O SH, Nam HJ, Go JM, Kim YH. A survey on the pesticide residues on agricultural products on the markets in Incheon area from 2003 to 2005. Korean J. Environ. Agr. 25: 180-189 (2006)
- Kim HY, Yoon SH, Park HJ, Lee JH, Gwak IS, Moon HS, Song MH, Jang YM, Lee MS, Park JS, Lee KH. Monitoring of residual pesticides in commercial agricultural products in Korea. Korean J. Food Sci. Technol. 39: 237-245 (2007)
- 3. Lee MG, Lee SR. Studies on Improve the Tolerance Setting System of Pesticide Residues in Foods. Korea Food & Drug Administration, Seoul, Korea. pp. 61-66 (2004)
- Kim CH. Review of disease incidence of major crops in 2000. Korean J. Pest. Sci. 5: 1-11 (2001)
- Lee MG, Hwang JM, Lee SR. The usage status of pesticides for vegetables under greenhouse cultivation in the southern area of Korea. Korean J. Pest. Sci. 9: 391-400 (2005)
- Joint UNEP/FAO/WHO Food Contamination Monitoring Programme. Guidelines for Predicting Dietary Intake of Pesticide Residues. World Health Organization, Geneva, Switzerland. pp. 8-15 (1989)
- Lee MG, Lee SR. Reduction factors and risk assessment of organophosphorus pesticides in Korean foods. Korean J. Food Sci. Technol. 29: 240-248 (1997)
- Kang SM, Lee MG. Fate of some pesticides during brining and cooking of Chinese cabbage and spinach. Food Sci. Biotechnol. 14: 77-81 (2005)
- Chun MH, Lee MG. Reduction of pesticide residues in the production of red pepper powder. Food Sci. Biotechnol. 15: 57-62 (2006)
- Christensen HB, Granby K, Rabolle M. Processing factors and variability of pyrimethanil, Fenhexamid, and tolyfluanid in strawberries. Food Addit. Contam. 20: 728-741 (2003)
- Boulaid M, Aguilera A, Camacho F, Soussi M, Valverde A. Effect of household processing and unit-to-unit variability of pyrifenox, pyridaben, and tralomethrin residues in tomatoes. J. Agr. Food Chem. 53: 4054-4058 (2005)
- Balinova AM, Mladenova RI, Shtereva DD. Effects of processing on pesticide residues in peaches intended for baby food. Food Addit. Contam. 23: 895-901 (2006)
- Rasmusssen RR, Poulsen ME, Hansen HCB. Distribution of multiple pesticide residues in apple segments after home processing. Food Addit. Contam. 20: 1044-1063 (2003)

¹⁾ When a pesticide was detected at below the LOQ, the processing factor was calculated using a half of the LOQ value and expressed as '<'.

- 14. Lee HD, You OJ, Ihm YB, Kwon HY, Jin YD, Kim JB, Kim YH, Park SS, Oh KS, Ko SL, Kim TH, Noh JG, Chung KY, Kyung KS. Residual characteristics of some pesticides in/on pepper fruits and leaves by different types, growing, and processing conditions. Korean J. Pest. Sci. 10: 99-106 (2006)
- KCPA. Agrochemicals Use Guide Book. Korea Crop Protection Association, Seoul, Korea (2005)
- KFDA. Food Standards Code. Korea Food & Drug Administration, Seoul, Korea. pp. 118-269 (2005)
- 17. Führ F. Fate of herbicide chemicals in the agricultural environment with particular emphasis on the application of nuclear techniques. pp. 99-106. In: Agrochemicals: Fate in Food and the Environment. June 7-11, Rome, Italy. International Atomic Energy Agency, Vienna, Austria (1982)
- Cabras P, Angioni A, Caboni P, Garau VL, Melis M, Pirisi FM, Cabitza F. Distribution of folpet on the grape surface after treatment. J. Agr. Food Chem. 48: 915-916 (2000)

- Tomlin CDS. The Pesticide Manual. 12th ed. British Crop Protection, London, UK (2000)
- Krol WJ, Arsenault TL, Pylypiw HM Jr, Mattina MJI. Reduction of pesticide residues on produce by rinsing. J. Agr. Food Chem. 48: 4666-4670 (2000)
- Angioni A, Schirra M, Garau VL, Melis M, Tuberoso CIG, Cabras P. Residues of azoxystrobin fenhexamid and pyrimethanil in strawberry following field treatments and the effect of domestic washing. Food Addit. Contam. 21: 1065-1070 (2004)
- Fernandez-Cruz M, Barreda M, Villarroya M, Peruga A, Llanos S, Garcia-Baudin JM. Captan an fenitrothion dissipation in fieldtreated cauliflowers and effect of household processing. Pest. Manag. Sci. 62: 637-645 (2006)
- Ambrus A, Solymosne ME, Korsos I. Estimation of uncertainty of sample preparation for the analysis of pesticide residues. J. Environ. Sci. Heal. B. 31: 443-450 (1996)