# ORIGINAL ARTICLE/RESIDUE and SAFETY

# An Extrapolation from Crop Classifications Based on Pesticide Residues Trial Data within Vegetables in Minor Crops

Jong-Hyouk Park, M. I. R. Mamun<sup>1</sup>, A. M. Abd El-Aty<sup>2</sup>, Jeong-Heui Choi, Geon-Jae Im<sup>3</sup>, Chang-Hwan Oh<sup>4</sup> and Jae-Han Shim\*

Natural Product Chemistry Laboratory, Division of Applied Bioscience and Biotechnology, College of Agriculture and Life Science, Chonnam National University, 300 Yong-Bong Dong, Buk-gu, Gwangju 500-757, Republic of Korea, <sup>1</sup>Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh, <sup>2</sup>Department of Pharmacology, Faculty of Veterinary Medicine, Cairo University, 12211-Giza, Egypt, <sup>3</sup>Pesticide Safety Division, National Institute of Agriculture Science and Technology, Rural Development Administration, Suwon, 441-707, Republic of Korea, <sup>4</sup>Department of Oriental Medical Food and Nutrition, Semyung University, Republic of Korea

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#### Abstract

An extrapolation of residue data of seven commonly used pesticides namely bifenthrin, chlorothalonil, cypermethrin, diazinon, fenvalerate, phenthoate and procymidone on a total of 22 minor crops has been carried out in an experimental field trial. The pesticides were applied to 11 leafy-, 5 root- and 6 stem-crops grown in the experimental green-house and the crops and plants were randomly collected at 1, 3, 5, 7 days after application. The average recoveries of applied pesticides were ranged from 72.0 to 117.0% in leafy crops, from 81.3 to 105.0% in stem crops and from 70.1 to 108.1% in the root-crops. Limits of detection (LODs) were 0.005-0.1 mg/kg in the leafy crops and 0.001-0.005 mg/kg in both the stem & root crops. Based on the results of residual dissipation pattern and their morphology, all crops were classified into high and low residual groups. The results showed that it might be possible to extrapolate residual data of stem-crops to root-crops within the same group. Crops that have currently no registered pesticide for use, would be possible to use the pesticides which are already been registered for the similar crops.

Key words minor crops, pesticide registration, dissipation of pesticides, MRLs

## Introduction

The withdrawal of pesticide registration for minor crop application has been a significant trend in the crop protection industry over the last decade. This is because of the potential sales of pesticides for pest control on fruits, vegetables, nuts, herbs and other minor crops are often so small that pesticide manufacturers are not willing to invest money to obtain an established Maximum Residue Limit (MRL) for these crops. Maximum Residue Limits (MRLs) represents the maximum quantity of residues in

the raw commodity of plants or animal origin which should reflect the use of minimum quantities of active substance necessary to achieve adequate pest control, applied in such a manner that the residues are as low as practicable and is toxicologically acceptable (EU Report, 1998). These values are normally fixed by the authorized body for crops for which the substances are registered. Unfortunately, due to the high cost for getting registration most of the pesticides have been registered for their use on major crops which produce high revenue. On the other hand, pesticides for minor uses are not always economically attractive for a pesticide registrant to maintain a small use of pesticide that produces low revenue (Ghidiu and Neary,

\*연락저자 : Tel. +82-62-530-2135, Fax. +82-62-530-0219

E-mail: jhshim@jnu.ac.kr

1994). As a result, limitations on the use of pesticides for minor crops are still a problem for the growers around the world and the problem is not so different in Korea.

There is no globally held definition of a minor crop. Those crops that are generally recognized as 'minor' grown on a relatively small area and commonly have a high value per unit area (Jarvis, 2003). For this reason minor crops are sometimes referred to as high value capacity crops. According to the reports of a federal-state project of USA known as Interregional Research Project No. 4 (IR-4), 11 million acres of minor crops are grown annually in the United States which have a combined value of \$32 billion and represent 42 percent of all crop sales (Senft, 1996; Dorschner *et al.*). These minor crops exceeded the value of all the other major crops including corn, cotton, soy-beans and wheat.

In the Republic of Korea, crops that are being cultivated on the lands below 1000 acres are called minor-crops. In recent years Korean farmers have started to grow a number of minor crops in green house all around the year in order to meet the off-season demand. But these growers have been facing the same problem about the lack of registered pesticides for minor crops and MRLs values without which they cannot cultivate their crops under Good Agriculture Practice (GAP). Although many arrangements have been/are being made to solve this problem in a number of states of the European Union and USA, it appears that the cost of extensive data requirements, mainly residues data, exacerbated by a lack of regulatory expertise in extrapolation, is often a major stumbling block (Bates, 2003; Perry, 2002).

Maximum Residues Limits are determined by taking into account the food intake, the average body weight of human being and pesticide residue levels under good agricultural practices which differ country to country depending on dietary customs. For this reason the MRL values of one pesticide for several foods are different in different countries. So, pesticide manufacturers have mainly focusing on their profit business always been paid attention to pesticides used for major crops and ignored the so-called 'minor-use' ones. In 1998, the Korean government implemented a national project called "pesticide registration trials for minor crops" under which a reasonable MRL

values for registered pesticides in or on minor crops were set as an output of the trial (Oh, 2001). But there are a number of minor crops growing in Korea for which no pesticide is registered by the companies. As a result, there is an uncertainty for the minor crops growing in Korea whether it will be accepted or not for marketing due to residue levels even in small amount present in the crops. Because Korean Food and Drug Administration (KFDA) adopts the lowest registered MRL value for a particular crop if a pesticide is not registered for a particular crop.

The system for setting maximum residue limits (MRLs) for so-called 'minor' crops is frequently based on simple extrapolation from values already set for superficially 'major' crops which reduces the necessity of performing additional field trial on pesticide/crop combinations (Reynolds, 2005). On the basis of existing knowledge and available data's, using the least favorable trial conditions, the residual behavior in/on plants or plants products is comparable under certain circumstances. In such cases, existing knowledge about the residue behavior in one situation can be transferred to another, and the scale of the trials for the comparable situation can be reduced, or trials may even be completely unnecessary (Working document EC, 2001). Taking the problem of unregistered pesticides for minor crops into consideration, the present study was designed to extrapolate residue trial data of seven pesticides on some minor crops in order to recommend MRL values comparing the data of major crops of same or similar group for which an MRL value has already been established.

Residual analysis of diazinon have been carried out in different matrices using gas chromatograph equipped with different detectors like GC-FTD (Flame Thermo ionic Detection, Albanis *et al.*, 1998), GC-NPD (Nitrogen Phosphorus Detection, Oliva *et al.*, 2000; Zapf *et al.*, 1995), GC-ECD (Electron-capture detector, Khay *et al.*, 2006; Correia *et al.*, 2000), GC-FID (Flame Ionization Detector, Bavcon *et al.*, 2003), GC-FPD (Flame Photometric Detection, Jongenotter *et al.*, 1999; Obana *et al.*, 2001), GC-MSD (Musshoff *et al.*, 2002) have earlier been reported. Determination of procymidone residues have previously been reported using GC-ECD (Navarro *et al.*, 2000; Bernal *et al.*, 1997), GC-NPD (Sanchez-Brunete *et al.*, 2002), GC-MS (Albero

et al., 2005; Pose-Juan et al., 2006), and GC-ECD followed by GC-MS equipped with a solvent-free solid injector was reported (Li et al., 2007).

Multiresidue analysis of organophosphorous and pyrethroid pesticides are commonly performed using GC-NPD (Nunes *et al.*, 1997). Multiresidue methods of cypermethrin, bifenthrin and fenvalerate utilizing GC-ECD have been reported (Sannino *et al.*, 2003) and GC-MS (Obana *et al.*, 2001; Columé *et al.*, 2001). Chlorothalonil and phenthoate was analyzed either together or in separate groups using GC-ECD (Chang *et al.*, 2005; Chen *et al.*, 2000) and GC-MSD (Chun *et al.*, 2003; Stan, 2000).

## Materials and Methods

#### Chemicals and reagents

Seven commonly used pesticides of commercial grade namely, cypermethrin, diazinon, procymidone, bifenthrin, chlorothalonil, fenvalerate, and phenthoate were purchased from the local market of Gwangju, Korea. Acetonitrile (Merck) and anhydrous sodium sulfate (Sigma) used in the extraction procedure were of pesticide grade.

## Field experiment and sampling

A total of 22 agricultural crops were selected for present study and divided into eleven leafy-, five root-and six stem-crops based on the shape of agricultural products and specific pesticide residues given by Korea Food and Drug Administration (KFDA) and from the result of pesticide residue monitoring in Agricultural Products in 2005 from the National Agricultural Products Quality Management (NAQS), Gwangju, Republic of Korea (Table 1).

All the selected crops were grown in the in-house experimental farm/green houses of the College of Agricultural and Life Science, Chonnam National University,

Table 1. Classification of twenty-two analyzed agricultural crops

Type	Class	Sub-class	Commodity (in Korean)
	Bulb		Chinese cabbage
	Non-bulb	Multiple harvest	chicory
			kale
			Korean lettuce
			whorled mallow
Leafy-crops (11)			Swiss chard
(11)			crown daisy
		Single harvest	geumgangcho
			Korean cabbage
			pak choi
			toscano leaf
			bonnet bellflower
_			carrot
Root-crops (5)			onion
(3)			radish (root)
			turnip (roots)
			celery
			dropwort-dry fields
Stem-crops			dropwort-rice paddy
(6)			leek
			stonecrop
			young radish

Gwangju, Republic of Korea. Leafy crops were sown in a dry field dropwort in a green house on a plot measuring 0.9 m x 1.4 m on 10 May, 2005 and the stem-crops were sown in a green house of the rice treatment complex on in rice paddy water dropwort whereas the root-crops in experimental plots of the practical Training Supervisory Board. Both the stem- and root crops were sown on 11 March 2006 on the plots of same size measuring 0.8 m x 1.2 m. The space between two cultivating rows in the growing filed was kept 0.2 m where same pesticide was sprayed and 0.4 m where different pesticides were sprayed.

The pesticides were divided into two groups according to their retention time and were sprayed once by a mechanical sprayer at a recommended dose when they grew up fully. The spraying concentrations and other information are given in the Table 2. The samples were collected randomly at 1, 3, 5 and 7 days after pesticide application. After harvesting, collected samples were chopped immediately, mixed, packed separately in plastic bags, labeled and stored at -20°C until analysis.

#### Sample extraction

Leafy crops

The samples were extracted by following the method "Korea Food Code No. 83" described in the guidebook by KFDA (2005). A 20-g representative sample of each leafy crop was homogenized with 50 mL acetonitrile for three minutes by a high-speed homogenizer (WiseMix<sup>TM</sup> HG-150, Daihan Scientific, Korea). The homogenate was suction-filtered through Whatman filtered paper (No. 6, England) and Celite 545 resting on a porcelain Büchner

funnel. The filtrate was then transferred to a separatory funnel (500 ml) in which 10 g of sodium chloride was added. The content was shaken for 1 min and allowed to stand for 30 min at  $4^{\circ}$ C. The organic phase was taken and evaporated to dryness at  $40^{\circ}$ C under vacuum.

#### Purification

The dry residue was dissolved in 2 ml (1 ml x 2 times) of 20% acetone in hexane (v/v) and subjected to clean up with a Solid-Phase Extraction (SPE) Florisil Cartridge (1 g). The florisil cartridge was activated by washing with 5 ml n-hexane followed by pre-equilibration by eluting 5 ml of 20% acetone in hexane (v/v). The sample was loaded to SPE cartridge and then eluted with 5 ml of 20% acetone in n-hexane (v/v) for collection. The effluent was evaporated under vacuum at  $40^{\circ}$ C to complete dryness and the dry residue was re-dissolved in 2 ml n-hexane (v/v) in a GC-vial for analysis.

Extraction procedure for stem— and root—crops A 40-g representative sample of each crops were homogenized with 100 mL acetonitrile for three minutes by a high-speed homogenizer (WiseMixTM HG-150, Daihan Scientific, Korea). The homogenate was suction-filtered through Whatman filtered paper (No. 6, England) and Celite 545 resting on a porcelain Büchner funnel. The filtrate was then transferred to a separatory funnel (500 ml) and was extracted by vigorously shaking with 100 ml of 50% dichloromethane in n-hexane (v/v) for two times (100 mL x 2). The organic phase was dehydrated over anhydrous sodium sulfate and the combined extract was

Table 2. Does of pesticides applied on the tested crop

Group	Pesticide	Class	Typical sales products (in Korean)	Applied dose
	Cypermethrin	Insecticide	Hoastak WP	20 ml/20 L H <sub>2</sub> O
I	Diazinon	Insecticide	Diaton EC	$20~ml/20~L~H_2O$
	Procymidone	Fungicide	Smileks WP	$20~g/20~L~H_2\mathrm{O}$
	Bifenthrin	Insecticide	Tasta WP	20 g/20 L H <sub>2</sub> O
П	Chlorothalonil	Fungicide	Dakonyl WP	32 g/20 L H <sub>2</sub> O
11	Fenvalerate	Insecticide	Smisaidim EC	$20~ml/20~L~H_2O$
	Phenthoate	Insecticide	Elsan EC	20 ml/20 L H <sub>2</sub> O

evaporated under vacuum to complete dryness.

#### Clean up

The dry residue was dissolved in 3 ml n-hexane and subjected to clean up with a Solid-Phase Extraction (SPE) Florisil Cartridge (1 g). The florisil cartridge was activated by washing with 5 ml n-hexane followed by conditioning with 5 ml of 20% acetone in hexane (v/v). The sample was loaded to SPE cartridge and then eluted with 15 ml of 20% acetone in n-hexane (v/v) for collection. The effluent was evaporated under vacuum at 40°C to complete dryness and the dry residue was re-dissolved in 2 ml n-hexane in a GC-vial for analysis.

Standard solution preparation and quantitative analysis Stock solution of a mixture of standard compounds were prepared in acetone by weighing approximately 0.01 g of each analyte into a 10 mL volumetric flask and diluting to obtain a concentration of about 1 mg/mL. Intermediate and working standard solutions were prepared by diluting the stock solutions with acetone. All the standard solutions were kept in dark centrifuge tubes and stored at -20°C.

#### Analytical conditions

#### Leafy-crops

A Hewlett Packard Gas Chromatograph 5890 Series II (USA) equipped with electron capture detector was used for the determination of pesticide residues in the leafy crops. Separations were carried out on a DB-5 column (30 m x 0.25 mm ID x 0.25 μm film thickness) with an operating condition having an oven temperature 200°C for 3 min, then increased to 300°C at 10°C/min, held at 300°C for 3 min. The temperature in the injection port and detector were 260°C and 280°C, respectively. Nitrogen was used as the carrier gas with a flow rate of 5 ml/min and split ratio was 14:1.

## Stem- and root-crops

An Agilent Gas Chromatograph 6890N (USA) equipped with ECD, a splitless capillary injector and an ultra-2 column (30 m x 0.25 mm ID x 0.25  $\mu$ m film thickness) were used for the detection and quantification of pesticide

residues in the root- and stem-crops. The temperature program of the oven was as follows:  $130^{\circ}\text{C}$  for 2 min, increased to  $180^{\circ}\text{C}$  at  $5^{\circ}\text{C/min}$  and hold for 10 min and then increased to  $290^{\circ}\text{C}$  at  $5^{\circ}\text{C/min}$  (hold 9 min) and finally increased to  $300^{\circ}\text{C}$  at  $5^{\circ}\text{C/min}$  and hold for 2 min. The injection port temperature was  $280^{\circ}\text{C}$  and the detector temperature was  $300^{\circ}\text{C}$ .

#### Recovery

Samples of untreated crops were spiked with appropriate amount of the standard solutions to reach the concentrations of 0.02 and 2.0 mg/kg for the leafy crops and 0.01 and 1.0 mg/kg for the stem and root crops. The samples were allowed to stand for 30 min prior to extraction following the same procedure described for the real samples. Three replicate analyses for each concentration were carried out.

## Results and discussion

### Method validation

Before analysis of the crop samples, the method was validated by extracting untreated samples from each kind of crops spiking in two different levels with each pesticides. The spiked levels of pesticides were from 0.02 to 2.0 mg/kg in leafy crops and that was from 0.01 to 1.0 mg/kg for the stem and root crops. The recoveries obtained for all the pesticides ranged from 72.0 to 117% in the leafy-, 81.3 to 105% in the stem- and 70.1 to 108% in the root-crops (Table 3). The recoveries were well acceptable in order to be supported by the international guidelines (SANCO, 2004) in which the mean recovery should fall within 70-110% in order to sufficiently validate the quantitative method.

Quantification was accomplished by using standard calibration curve prepared by diluting the stock solutions in acetone. According to standard calibration curves, the concentrations of the tested pesticides were ranged from 0.04 to 150 ng and the linearity achieved by all pesticides with correlation coefficients ranged from 0.962 to 1.0 in the leafy crops, from 0.978 to 0.999 in the root- and

Table 3. Recovery values and limit of detections (LODs) of the pesticides spiked in control sample

Crop	Pesticide	Spiking level (mg/kg)	Recovery* (%)	LOD (mg/L)
Leafy-Crop	Diazinon	0.10-0.38	75.04±5.31-91.33±1.60	0.005
	Procymidone	0.05-0.19	71.98±2.20-88.64±21.50	0.001
	Cypermethrin	0.10-0.38	87.43±7.70-88.64±21.50	0.005
	Bifenthrin	0.02-0.10	81.98±4.50-95.13±13.30	0.005
	Chlorothalonil	0.10-0.50	87.27±9.20-84.17±5.80	0.025
	Fenvalerate	0.10-0.50	$88.77 \pm 14.20 - 94.25 \pm 1.60$	0.025
	Phenthoate	0.40-2.00	96.54±21.10-117.42±35.30	0.100
Root-Crop	Diazinon	0.10-1.00	95.60±1.76-104.00±1.74	0.005
	Procymidone	0.02-0.20	99.60±1.76-102.00±1.74	0.001
	Cypermethrin	0.10-1.00	99.30±1.64-99.00±1.74	0.005
	Bifenthrin	0.01-0.30	$70.67 \pm 1.53 - 99.00 \pm 1.74$	0.002
	Chlorothalonil	0.02-0.20	$70.10\pm2.20$ - $98.17\pm~1.74$	0.001
	Fenvalerate	0.02-0.20	79.22±2.20-92.00±1.74	0.002
	Phenthoate	0.02-0.10	84.33±1.75-108.15±1.74	0.001
Stem-Crop	Diazinon	0.10-1.00	91.33±1.60-92.67±5.13	0.005
	Procymidone	0.02-0.20	85.10±6.62-100.37±0.96	0.001
	Cypermethrin	0.10-1.00	91.33±1.60-101.57±0.96	0.005
	Bifenthrin	0.10-1.00	91.33±1.60-101.57±0.96	0.005
	Chlorothalonil	0.02-0.20	98.33±1.60-105±5.74	0.001
	Fenvalerate	0.01-0.10	81.33±1.60-99.33±1.75	0.001
	Phenthoate	0.02-0.20	88.64±5.50-99.30±1.64	0.002

<sup>\*</sup> Recovery was analyzed three times in each low and high spiked concentration.

0.988 to 1.0 in the stem crops. The limits of detections were from 0.001 to 0.1 mg/kg (Table 3). The analytical methodology, therefore, was reliable and allowed the correct determination of pesticides residues in real samples and also is used to determine recoveries to check out the sample extraction procedures and analytical instrument conditions.

## Residual ratio (%)

In this study in order to classify the crops into high and low residual group, we have calculated the percent residual ratio of each pesticide using the residue values obtained and the active ingredient present in the commercial products. Because the crop classifications are generally done by the dissipation pattern of pesticides on the agricultural commodities as the active ingredients are different from each other in the commercial formulations. In case of procymidone, the calculation was done separately as it

has a systemic action. The percent residual ratios of all pesticides in each crop were calculated at 1, 3, 5, and 7 day after spraying. The results are shown in Table 4 and 5 which shows that the residues of the applied pesticides in all crops were found to be lower than MRL values at seven day after treatment.

The residual dissipation pattern of pesticides in crops harvested at each day after spraying shows from Fig. 1 to Fig. 3. From the point of overview on the behavior of pesticides in all crops at each day after spraying, it can be seen that the maximum residual ratio was found in kale at 1 day, and in crown daisy at 3, 5, and 7 day, both belong to the leafy-crops. Whereas, the minimum were found in onion belongs to the root-crops at all days after spraying.

The percent residual ratio at 1 day after spraying was maximum in kale and the minimum was in pak choi. The residual ratio (%) at 3 day after spraying was maximum in crown daisy and minimum in pak choi whereas at another

two *i.e.* at 5 and 7 days the maximum was again in crown daisy and the minimum was in Korean cabbage (Fig. 1).

Similarly, in the group of root-crops (Fig. 2), the maximum residual ratio at 1 day after spraying was in radish and the minimum were in onion. A little increase in residual ratio in onion at day 3 might have arisen due to mishandling of sampling. The results from the group of stem-crops (Fig. 3) show that the maximum residual ratio was in young radish at 1 day and in leek at 3, 5, and 7 day after spraying. Whereas the minimum residual ratio (%) was in leek at 1 day, in dropwort-rice paddy at 3 and 5 day and in stonecrop at 7 day after spraying.

The residual ratios were decreased gradually for most

leafy-crops except for the crown daisy and kale in which the ratio decreased dramatically within 3 days. The residual ratios were decreased gradually in all the stem- and rootcrops within 3 days, except in radish where it decreased dramatically.

The results of residual ratios are shown in Fig. 4, 5, & 6 as bar graphs. In leafy-crops (Fig. 4) the maximum residual ratio was crown daisy (15.41%), whereas the minimum residual ratio was Chinese cabbage (2.45%). Bonnet bellflower (0.71%) was found in the maximum residual ratio and onion (0.26%) was the minimum in root-crops (Fig. 5). Whereas leek and stonecrop were recorded the maximum and minimum residual ratio in

Table 4. Pesticide residual ratio in leafy-crops at harvest

G.		Residual ratio (%) at the	day after treatment (day)	1
Crop	1	3	5	7
Crown daisy	89.28±1.23	46.12±1.87	38.94±3.12	15.41±1.56
Korean lettuce	24.44±1.98	25.32±2.34	16.84±1.45	12.93±0.90
Geumgangcho	34.15±2.12	18.90±4.35	15.77±2.34	10.88±0.28
Whorled mallow	$21.78\pm0.90$	18.86±5.67	12.72±4.12	$10.84 \pm 0.32$
Chicory	14.85±0.67	$20.89\pm6.71$	12.35±2.34	9.93±1.94
Toscano leaf	$36.68 \pm 0.68$	21.47±3.45	9.57±2.12	7.91±0.68
Kale	90.64±3.45	$28.06 \pm 2.76$	11.02±1.56	5.80±1.81
Swiss chard	13.13±2.12	12.37±4.12	10.01±2.54	4.54±0.36
Korean Cabbage	21.03±3.12	10.21±2.32	8.76±3.42	3.83±0.26
Pak choi	10.67±2.12	9.72±2.34	7.45±2.89	$2.62\pm0.24$
Chinese cabbage	15.67±1.09	11.23±1.56	3.25±2.56	2.45±0.18

Table 5. Pesticide residual ratio in root- and stem-crops at harvest

Class	Crop —	R	esidual ratio (%) at the	day after treatment (da	ny)
		1	3	5	7
Root-crop	Carrot	0.76±0.02	0.62±0.01	0.65±0.00	0.55±0.01
	Turnip (roots)	$0.97 \pm 0.02$	$0.89\pm0.00$	$0.71 \pm 0.00$	0.45±0.01
	Onion	$0.41\pm0.03$	$0.61\pm0.00$	0.33±0.00	$0.20\pm0.02$
	Radish (roots)	$1.92\pm0.01$	$0.84 \pm 0.00$	$0.70\pm0.00$	$0.26 \pm 0.01$
	B. bellflower	$0.82\pm0.01$	1.28±0.00	1.11±0.00	$0.71 \pm 0.01$
Stem-crop	Dropwort- rice paddy	65.78±0.12	30.11±1.12	16.55±0.12	11.65±1.12
	Dropwort- dry fields	70.30±0.23	33.27±4.12	25.53±0.19	10.71±1.14
	Stonecrop	57.20±0.24	33.08±3.12	20.27±0.62	$8.60\pm1.09$
	Leek	55.20±1.89	44.02±8.62	35.47±0.92	18.36±1.45
	Celery	85.84±0.68	33.64±1.12	24.75±0.98	10.93±0.87
	Young radish	91.14±1.23	34.89±6.12	28.88±0.62	15.33±1.01

stem-crops (Fig. 6).

At the all days after spraying, the residual ratio in leafy-crops had broadest scope in other crop classes, the reason might be due to the various shape of them. Whereas in root-crops the residual ratio was minimum might be due to the pre-treatment done on them by washing and peeling off after collection from the field.

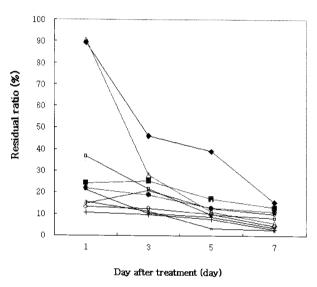


Fig. 1. All pesticides residual ratio (%) in each leafy-crops harvested at 1, 3, 5, and 7 days after application: crown daisy ♠, Korean lettuce ■, geumgangcho ♠, whorled mallow ♠, chicory ♦, toscano leaf □, kale △, Swiss chard ○, Korean cabbage ■, pak choi +, Chinese cabbage ×.

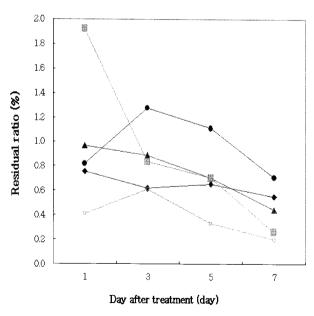


Fig. 2. All pesticides residual ratio (%) in each root-crops harvested at 1, 3, 5, and 7 days after application: carrot  $\spadesuit$ , turnip  $\spadesuit$ , onion  $\square$ , radish (root)  $\blacksquare$ , bonnet bellflower  $\blacksquare$ .

All the crops were classified into two groups called 'high residue' and 'low residue' according to the dissipation rates of pesticides residues by 50% windows in each crops collected at only 7 day after application. Crown daisy, Korean lettuce, geumgangcho, whorled mallow and chicory were of high residual group. At the same

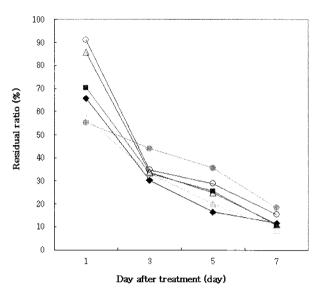
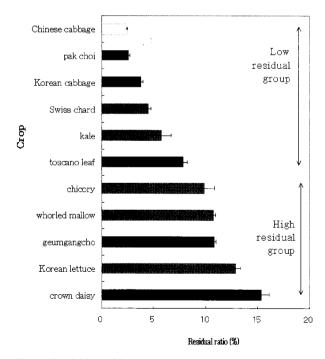


Fig. 3. All pesticides residual ratio (%) in each stem-crops harvested at 1, 3, 5, and 7 days after application: dropwort-rice paddy ♠, dropwort-dry fields ■, stonecrop ♠, leek ♠, celery △, young radish ○.



**Fig. 4.** Pesticide residual ratio in leafy-crops at 7th day after treatment: Bulb □, Non-bulb (multiple harvest) ■, Non-bulb (single harvest) ■.

time, toscano leaf, kale, Swiss chard, pak choi, Chinese cabbage and Korean cabbage were found to be in the low residual group (Table 6).

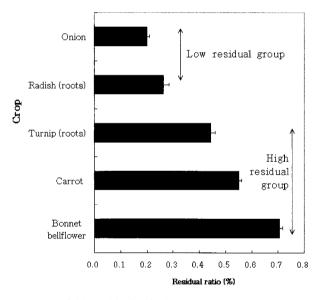
Among the root- and stem crops, the pesticides dissipated in shorter time in all root crops than in the stem crops. Turnip (roots), carrot and bonnet bellflower of root-crops and young radish along with leek of stem-crops fell into high residual group. In contrast, onion and radish (roots) of root-crops and dropwort-rice paddies, celery, dropwort-dry fields and stonecrop of stem-crops fell into low residual group. In this study, leek, dry fields-water dropwort, carrot, and radish were the representative crops and representative pattern in the residual dissipation of corresponding group.

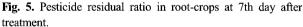
Where there are similar registered use patterns and MRLs, or residues data for more than one member of a crop

group, then an MRL can be established that applies to each member of the crop group. These known as "Group MRLs". Crop groups are groups of closely related commodities which are classified by similar characteristics and residues potential. A group MRL allows the use of a product to be approved on any member of the crop group, where similarity in use pattern can be adequately demonstrated and residues data are provided for representative members of the group (NRA Information Sheet, 2000).

## Conclusion

An extrapolation study from crop classifications based on pesticide residues trial data within vegetables in 22 minor crops with seven commonly used pesticides was carried out successfully. It could be concluded from the





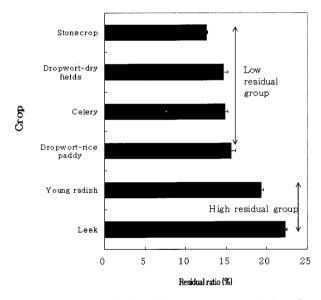


Fig. 6. Pesticide residual ratio in stem-crops at 7th day after treatment.

Table 6. Crop classification for the minor-crops based on pesticide residues dissipation pattern of in-house and field trial

Class	Residual ratio (%)			
Class	High residual group	Low residual group		
Leafy	crown daisy, chicory Korean lettuce*,	toscano leaf, kale, Swiss chard, Chinese cabbage,		
-crop	geumgangcho, whorled mallow	pak choi, Korean cabbage*		
Root	bonnet bellflower, carrot*, turnip (roots)	radish (roots)*, onion		
-crop	bonnet bennower, carrot, turnip (roots)			
Stem	look voying modich*	dropwort-rice paddy, dropwort-dry fields*, celery,		
-crop	leek, young radish*	stonecrop		

<sup>\*</sup> This crops were represented pattern of each group.

result obtained in this study that, it might be possible to extrapolate residual data of stem-crops from the data of root-crops within same group and that crops that have currently no registered pesticide for use, would be possible to use the pesticides which are already been registered for the similar crops combining the information about the morphology, growth characteristic, residual trial data, crop processing factor, and Acceptable Daily Intake (ADI).

The information obtained from this study might be considered as recommendations by RDA in order to help making new policies. Pesticide manufacturers would be benefited by selling the products to growers of varieties of minor crops which would led the growers to have a broader selection of pesticides in order to combat peat problems and increase the quality and yield of the products. On the other hand, this would help to reduce the cases of MRL-violation which were being reported via news media in Republic of Korea. Materialization of these recommendations will help facilitation of the registration of new pesticides for minor crops at significantly lower cost which will ultimately help the government, pesticide manufacturers and the people Republic of Korea in order to have safe food.

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## 소면적 재배작물의 농약 잔류성 시험 후 작물 그룹화를 통한 외삽적용

박종혁·M, I, R, Mamun<sup>1</sup>·A, M, Abd El-Aty<sup>2</sup>·최정희·임건재<sup>3</sup>·오창환<sup>4</sup>·심재한\*

- 전남대학교 응용생물공학부, <sup>1</sup>Department of Chemistry, University of Dhaka, <sup>2</sup>Department of Pharmacology, Faculty of Veterinary Medicine, Cairo University, <sup>3</sup>농촌진흥청 농업과학기술원, <sup>4</sup>세명대학교 한방식품영양학부
- 요 약 Bifenthrin, chlorothalonil, cypermethrin, diazinon, fenvalerate, phenthoate 및 procymidone 등 7종의 농약에 대한 잔류시험을 통해 외삽적용을 위한 연구를 실시하였다. 실험을 위해 소면적 재배작물 중 잔류농약 부적합 사례가 많은 작물을 중심으로 11종의 엽채류, 5종의 근채류, 그리고 6종의 경채류를 포함한 총 22종의 작물을 선정하여 재배한 후 7종의 농약을 각각 처리하여 24시간 경과 시점을 1일로 하여 1, 3, 5, 7 일차에 수확하여 분석하였다. 실험결과 회수율은 엽채류는 72.0~117.0%, 경채류는 81.3~105.0%, 그리고 근채류는 70.1~108.1% 수준이었고 검출한계는 엽채류는 0.005-0.1 mg/kg, 경채류와 근채류는 0.001-0.005 mg/kg 수준이었다. 농약의 감소경향과 작물의 표면 형태학적 차이에 의한 농약 잔류특성을 파악 비교하여 선정된 작물을 고잔류군과 저잔류군으로 그룹화하였고 이 내용을 바탕으로 대상 농약들에 대하여 경채류 및 근채류 작물을 대상으로 농약데이터의 외삽을 통한 안전사용기준 및 MRL의 설정이 가능할 것으로 판단된다.

색인어 소면적 재배작물, 농약 등록, 농약잔류, 잔류허용기준