

Comparative Persistence of Pesticides on Selected Cultivars of Specialty Vegetables

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The behavior and dissipation of several pesticides on selected cultivars of specialty vegetable crops were compared to determine appropriate preharvest intervals for compliance with maximum residue limits. To reduce application variability, a tank mix of pesticides was applied for each trial. Residues of eight pesticides applied to bok choy, Chinese broccoli, and fuzzy squash were similar for the two leafy vegetables; residues were higher than on squash because of the latter's larger mass-to-surface area ratio. Whereas residues of five of the nine pesticides applied to cabbage, Chinese cabbage, and bok choy did not differ significantly from 3 to 14 days after application, residues of cypermethrin and three fungicides were significantly higher on Chinese cabbage and bok choy. The residue deposits of the pesticides were about 50% lower on Chinese cabbage and 90% lower on cabbage than on bok choy. Dissipation of residues on different cultivars of lettuce and cabbage were compared after application of nine pesticides. With the exception of captan, residues on head lettuce were lower than on the other lettuces on day 1; cultivar differences were not significant for most of the nine applied pesticides on days 3 and 8. Generally, residues of the nine individual pesticides on storage cabbage, savoy cabbage, Chinese cabbage, and tah tsai did not differ significantly from day 1 to day 7 after application. Residue concentrations were generally significantly higher on bok choy than on the other cultivars. Residue deposits generally correlated with the rate of application; residues of captan, however, were about 50% of the predicted value. Significant differences in deposit and dissipation were observed among cultivars and pesticides, with dramatic initial decreases for diazinon and parathion. Because of their higher exposed surface area-to-mass ratios, leafier crops had higher residue concentrations than head varieties. Residues on lettuce cultivars were higher than on the cabbages. The results clearly indicate that structure significantly affects residue deposit and dissipation, and pesticide recommendations cannot always be extended to specialty crops without an investigation of the changes in preharvest intervals to prevent violations of the maximum residue limits.

KEYWORDS: Pesticide dissipation; lettuce; cabbage; Chinese vegetables

INTRODUCTION

The Ontario commercial vegetable industry has recently diversified to include many different types of vegetables, in particular those of Asian and Middle Eastern origin. These specialty crops, such as Chinese cabbage and Chinese radish, were originally produced by smaller growers and were sold directly to oriental restaurants and ethnic communities. Today, demand has increased as a result of cultural and demographic changes in Canada, and ethnic vegetables are widely available through domestic and import sources (1, 2). Traditionally, the Ontario lettuce and cabbage industries consisted mainly of

cultivars such as crisphead lettuce and fresh, storage, kraut, and processing cabbage. Today, many lettuce cultivars are grown including, romaine or cos, green bibb, buttonhead, Boston, and looseleaf types. Many brassicae, such as Chinese cabbage, nappa, savoy, and michihli types, are in wide production. In Canada, consumption of fresh vegetables, excluding potatoes, has been increasing steadily over the past 25 years, with lettuce ranking first and cabbage fifth (3, 4).

About 1000–1400 ha of oriental vegetables are grown in Ontario with an estimated farm value in excess of \$12 million (5). These ethnic vegetables are grown on small farms of 5–100 ha; up to three crops per growing season are produced and marketed locally. Many of these crops are grown in small blocks that are planted in succession and harvested daily throughout the growing season (snow peas, Chinese broccoli, choy sum), whereas others (headed cabbage) require most of the growing season to mature (6).

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Table 1. Leaf and Growth Characteristics of Selected Lettuce and Cabbage Cultivars

common name and cultivar		characteristics
	brassica	
cabbage (Survivor)		external leaves completely cover internal leaves
savoy cabbage (Primavoy)		external leaves cover internal leaves
Chinese cabbage (Kasumi)		nappa type, upright barrel-shaped heads
thick mustard cabbage (Bok Choi)		Chinese leaf cabbage, heavy leaves
Shanghai pak choi (Mei Quing Choi)		thin petiole, upright, spoon-shaped leaves
non-heading Chinese cabbage (Tah Tsai)		low compact spoon-shaped leaves
	lettuce and kale	
head lettuce (Ithaca)		external leaves completely cover internal leaves
romaine lettuce (Parris Island Cos)		medium tall, upright, cylindrical heads
looseleaf (Grand Rapids)		open heads
endive (Green Curled)		finely cut and curled fringed leaves
butterhead lettuce (Buttercrunch)		bibb type, crisp thick leaves
kale (Green Curled Scotch)		bushy plant, curled leaves

Pesticides are often registered on major crops, whereas many of the lesser-grown, but economically important, specialty crops lack crop-protection chemicals. Several low-hectare or so-called minor crops are closely related to those grown on a much larger scale and are infested by similar pests (7). The first comprehensive survey of pests on oriental cruciferous vegetables in southern Ontario was completed in 1998 (5), and only recently have some of these crops received crop protection recommendations (8, 9). In the absence of effective recommendations, growers of minor crops tend to use pesticides that are recommended for the major related crops (7). A monitoring survey for pesticide residues on fruits and vegetables produced in Ontario from 1991 to 1995 (10) revealed low concentrations of nonrecommended pesticides in many of the specialty crops, often leading to violations of the maximum residue limits (MRLs) permitted under the *Canadian Food and Drugs Act and Regulations* (11). Where no specific MRL is listed, a value of 0.1 mg/kg is designated as the adulteration limit. For specialty crops, Health Canada uses the MRL for a closely related major commodity; for example, the MRL for cabbage is used for bok choi, pak choi, and sui choi, and that for spinach or celery is used for ong choi.

Different cultivars of lettuce and brassica crops can have distinctive leaf form, shape, and growth characteristics; individual pesticides might exhibit different dissipation rates after application to different cultivars of each crop. Cabras et al. (12) noted that foliar application, but not soil treatment, resulted in residue concentrations on lettuce that were affected by the growth habit of the lettuce. Sances et al. (13) reported that the highest concentrations of cypermethrin occurred on the basal and exterior wrapper leaves of head lettuce. Additionally, variations in plant growth, geographical location, or weather can affect dissipation rates and harvest residues (14, 15).

Because major differences exist in the growth and leaf characteristics of many specialty crops (Table 1), the potential for MRL violations exists. It is important to confirm that current crop recommendations for major commodities are acceptable and that, when extended to minor commodities, the recommended preharvest interval (PHI) is sufficient to reduce residues at harvest below the MRL. In this study, the dissipation of several pesticides was examined over a period of 14 days on bok choi (thick mustard cabbage), Chinese cabbage, Chinese broccoli, fuzzy squash, and snow peas to determine appropriate PHIs. In addition, a comparative dissipation study with nine pesticides examined the effect of cultivars of various lettuce and cabbage varieties.

MATERIALS AND METHODS

Field Experiments. Seeds were purchased from Stokes Seed Co. (St. Catharines, Ontario, Canada). Studies on Chinese broccoli, bok choi, fuzzy squash, cabbage, and Chinese cabbage and the lettuce and cabbage cultivar experiments were undertaken at the University of Guelph Muck Crops Research Station (MCRS), Holland Marsh, Kettleby, Ontario, Canada, on muck soil (ca. 72% organic matter). Treatments at the MCRS were applied with a tractor-mounted sprayer with overhead fan T-jet nozzles spaced 50 cm apart, delivering 550 L/ha of spray mixture at 500 kPa. The snow pea study was located at the University of Guelph Cambridge Research Station, Cambridge, Ontario, Canada, on Fox sandy loam. The tractor-mounted sprayer was equipped with a boom sprayer with three fan T-jet nozzles, one overhead nozzle, and two drop nozzles for each row, delivering 800 L/ha of spray mixture at 415 kPa. Field samples were prepared according to normal harvesting practices, i.e., cutting the plant off at soil level and removing loose outer leaves. Each replicate of each crop was placed in a separate bag, sealed, and delivered fresh, within 2 h, to the laboratory for extraction and analysis.

Chinese Broccoli, Bok Choi, and Fuzzy Squash. Chinese broccoli (Guy Lon), thick mustard cabbage (Bok Choi) and fuzzy squash (Mao Gwa) were transplanted in four-row plots, 7 m long, replicated four times. Endosulfan (Thiodan 4 EC) 0.8 kg of AI/ha, dimethoate (Cygon 480 EC) 0.48 kg of AI/ha, pirimicarb (Pirimor 50 WP) 0.25 kg of AI/ha, malathion (Malathion 25% WP) 1.1 kg of AI/ha, phosmet (Imidan 50% WP) 1.1 kg of AI/ha, fenvalerate (Belmark 300 EC) 0.10 kg of AI/ha, permethrin (Ambush 500 EC) 0.07 kg of AI/ha, and iprodione (Rovral 50 WP) 0.75 kg of AI/ha were applied as a tank mix. The crops were treated prior to harvest and sampled when mature at 0, 1, 3, 7, 10, 15, and 21 days after application for bok choi, and at 0, 3, 7, and 13 days for Chinese broccoli and fuzzy squash. Four heads of bok choi, six stalks of Chinese broccoli, and four medium-sized fuzzy squash were harvested from each replicate.

Cabbage, Chinese Cabbage, and Bok Choi. Cabbage (Survivor), Chinese cabbage (Kasumi) and thick mustard cabbage (Bok Choi) were transplanted in two rows, 8 m long, replicated four times. A tank mix of diazinon (Diazinon 500 EC) 0.25 kg of AI/ha, parathion (Parathion 960 EC) 0.26 kg of AI/ha, endosulfan (Thiodan 400 g/L) 1.1 kg of AI/ha, iprodione (Rovral 50 WP) 1.0 kg of AI/ha, captan (Captan 80 WP) 3.4 kg of AI/ha, cypermethrin (Cymbush 250 EC) 0.07 kg of AI/ha, carbofuran (Furadan 480 F) 0.53 kg of AI/ha, metalaxyl (Ridomil 240 EC) 1.0 kg of AI/ha, and mancozeb (Dithane DG 75%) 2.0 kg of AI/ha was applied. All crops were treated prior to harvest and sampled when mature at 0, 1, 3, 7, 10, and 14 days after application. Cabbage cultivars were harvested with the interior and exterior wrapper leaves intact and the senescent basal leaves removed; four heads per replicate were harvested.

Chinese Broccoli. Chinese broccoli (Guy Lon) was transplanted in three-row plots, 6 m long, replicated four times. Diazinon (Diazinon 500 EC), permethrin (Ambush 500 EC), and cypermethrin (Ripcord 400 EC) were applied as a tank mix at the rates of 750, 70, and 50 g of AI/ha, respectively. The crop was treated prior to harvest and sampled

when the crop was mature at 0, 1, 3, 8, 10, and 14 days after application. Six stalks were harvested for each replicate.

Snow Peas. Snow peas (Ho Lohn Dow) were seeded in two-row plots, 6 m long, replicated four times. Dimethoate (Cygon 480 EC), malathion (Malathion 25% WP), and mancozeb (Dithane M45 50% WP) were applied as a tank mix at the rates of 1.7, 1.1, and 2.0 kg of AI/ha, respectively. The crop was treated prior to harvest and sampled during harvest maturity at 0, 1, 3, 7, 10, and 14 days after application.

Comparative Dissipation on Lettuce and Cabbage Cultivars. Head lettuce (Ithaca), romaine lettuce (Parris Island Cos), looseleaf (Grand Rapids, open head), endive (Green Curled), butterhead lettuce (Buttercrunch), kale (Green Curled Scotch), cabbage (Survivor), savoy cabbage (Primavoy), Chinese cabbage (Kasumi), thick mustard cabbage (Bok Choi), non-heading Chinese cabbage (Tah Tsai), and Shanghai pak choi (Mei Quing Choi) were seeded and later transplanted on different dates so that all of the crops could be harvested at the same time. Each plot consisted of two rows, 8 m long, replicated four times. A tank mix of diazinon (Diazinon 500 EC) 0.25 kg of AI/ha, parathion (Parathion 960 EC) 0.26 kg of AI/ha, endosulfan (Thiodan 400 g/L) 1.1 kg of AI/ha, iprodione (Rovral 50 WP) 1.0 kg of AI/ha, captan (Captan 80 WP) 3.4 kg of AI/ha, cypermethrin (Cymbush 250 EC) 0.07 kg of AI/ha, carbofuran (Furadan 480 F) 0.53 kg of AI/ha, metalaxyl (Ridomil 240 EC) 1.0 kg of AI/ha, and mancozeb (Dithane DG 75%) 2.0 kg of AI/ha was applied. The crops were treated prior to harvest and sampled when mature at 1, 3, and 8 days after application for the lettuce cultivars and at 1, 3, and 7 days for the cabbage cultivars. Plants were harvested with interior and exterior wrapper leaves intact and senescent basal leaves removed. Four to six half-heads per replicate plot or complete heads for smaller cultivars were taken from the two rows.

Analytical Methods. Samples were composited in a Hobart food chopper, and a 50-g subsample was analyzed as described by Burchat et al. (16). The sample was blended with 200 of mL 2:1 acetonitrile/water and filtered. A half-aliquote was diluted with water and saturated NaCl solution, and partitioned twice into dichloromethane, dried through sodium sulfate, concentrated just to dryness, and redissolved in hexane. A portion of the extract was cleaned and fractionated on Florisil according to the method of Mills et al. (17) as described by Braun and Stanek (18). Endosulfan, the pyrethroids, and captan were determined by capillary column gas chromatography (GC) with electron capture detection. The organophosphorus insecticides were determined in the extract without cleanup using capillary column GC with flame photometric detection, whereas the nitrogen-containing compounds (carbofuran, iprodione, metalaxyl, and pirimicarb) were determined by capillary column GC with a nitrogen-phosphorus detector (NPD). For mancozeb determination, a 10–100-g subsample was analyzed using the carbon disulfide evolution method (19, 20). Recoveries ranged from 70 to 135% and were more variable with the NPD. The detection limits were 0.001 mg/kg for endosulfan and malathion; 0.005 for captan, diazinon, parathion, phosmet, metalaxyl, and the pyrethroid insecticides; 0.01 for carbofuran, pirimicarb, and iprodione; and 0.1 for mancozeb.

Statistical Analysis. The LSD test (using SAS) was used to determine significant differences between the data. One-half of the detection limit was used when the residue was not detected. Correlations were determined using Excel.

RESULTS AND DISCUSSION

Many factors contribute to pesticide deposit and residue dissipation, but under similar environmental conditions, the crop (morphology, cuticle characteristics, stage of growth at treatment, growth rate) and application method (formulation, rate, water volume, pressure, nozzle type, and boom height above canopy) are most important (15, 21). To control some of these factors, pesticides were applied in various tank mixes to the different crops, thus eliminating application variations, although the combination might affect the persistence of some of the chemicals (22–24). Pesticides were selected to represent different classes of commonly used pesticides with a range of vapor pressures and water solubilities. In the lettuce and cabbage

cultivar trials, the various cultivars were transplanted to mature at the same time. Simultaneous application then permitted a comparison of dissipation on the cultivars under the same weather conditions. The pesticides were applied as a tank mix on cabbage and lettuce cultivars to investigate whether the MRL and the PHI for cabbage would be suitable for bok choi, Chinese cabbage, tah tsai, mei quing choi, savoy, and michihli types and whether those for head lettuce would be appropriate for romaine, butterhead, Boston, and looseleaf types, as well as endive and kale.

In the trial with bok choi, Chinese broccoli, and fuzzy squash (Table 2), the initial residue deposit of the eight individual pesticides on each crop correlated well with the application rate, except for malathion and phosmet on fuzzy squash. Similar deposits were observed for the two leafy vegetables and were substantially higher than those determined on fuzzy squash because of its high mass-to-surface area ratio. Residues of the two pyrethroids were below the detection limit on fuzzy squash even on the day of application. For bok choi, all of the residue dissipations exhibited a first-order kinetic decline ($R^2 > 0.91$) with half-lives ranging from 1.3 to 4.1 days. Malathion declined rapidly after application and had the shortest half-life, followed in increasing persistence by pirimicarb, phosmet, dimethoate, fenvalerate, iprodione, endosulfan, and then permethrin, a relationship that generally correlates with their vapor pressures.

For bok choi, the residue of each pesticide was not significantly different for days 7–21, with the exception of endosulfan, permethrin, and fenvalerate (Table 2). For Chinese broccoli and fuzzy squash, the individual residues from day 3 to day 13 were not significantly different, except for endosulfan, permethrin, and iprodione on Chinese broccoli and pirimicarb on fuzzy squash. The Ontario recommendations (9) of a 4-day PHI for dimethoate on broccoli and cabbage, a 3-day PHI for permethrin on cabbage, a 7-day PHI for permethrin on broccoli, and a 7-day PHI for endosulfan on cole crops were suitable to meet the MRLs of 2, 0.5, 0.5, and 2 mg/kg, respectively. Residues of dimethoate, endosulfan, and permethrin on both bok choi and Chinese broccoli were below permitted MRLs if that crops were harvested at the recommended preharvest intervals. Fenvalerate on bok choi was below the MRL of 0.1 by the 14-day PHI. Malathion is not recommended for use on cabbage and broccoli but has MRLs of 6 and 0.5 mg/kg, respectively, on the two crops; residues on bok choi and Chinese broccoli were below this MRL by days 1 and 3, respectively. Residues of the remaining pesticides on bok choi and Chinese broccoli were less than the 0.1 mg/kg residue limit by days 7 and 3 for pirimicarb, days 15 and 13 for phosmet, and days 21 and 13 for iprodione. Endosulfan and malathion are recommended for foliar application on squash with MRLs of 1 and 3 mg/kg and PHIs of 2 and 3 days, respectively; residues on fuzzy squash were below the MRL by the recommended preharvest interval. The remaining pesticides were below 0.1 mg/kg on the day of application, except for iprodione, which required 7 days to decline below 0.1 mg/kg.

Initial residue deposits on the three cabbage crops (Table 3) correlated well with the application rate, except for mancozeb on bok choi, metalaxyl and captan on cabbage, and metalaxyl and iprodione on Chinese cabbage. In general, initial residue deposits were about 50% lower on Chinese cabbage and 90% lower on cabbage relative to those on bok choi. The growth habits of Chinese cabbage (nappa type, upright barrel-shaped heads) and bok choi (Chinese leaf cabbage, heavy leaves) are similar and quite different from those of the denser cabbage (Survivor), where the external leaves completely cover the

Table 2. Pesticide Residues in Bok Choi, Chinese Broccoli, and Fuzzy Squash^a

days after application	rate	residue (mg/kg) ^b for indicated pesticide							
		dimethoate	malathion	phosmet	endosulfan	permethrin	fenvalerate	pirimicarb	iprodione
		0.48	1.1	1.1	0.8	0.07	0.1	0.25	0.75
bok choy									
	MRL	2.0/4	6.0	0.1	2.0/7	0.5/3	0.1/14	0.1	0.1
0		3.1 a ^c	9.5 a	10. a	5.9 a	0.67 a	1.6 a	1.4 a	4.8 a
1		2.0 b	5.0 b	6.9 b	3.7 b	0.56 a	1.2 b	0.67 b	4.2 a
3		1.0 c	0.32 c	1.9 c	2.4 c	0.32 b	0.81 c	0.28 c	1.9 b
7		0.22 d	0.039 c	0.38 cd	1.3 d	0.15 c	0.33 d	0.064 d	0.63 c
10		0.12 d	0.010 c	0.17 d	0.80 de	0.070 cd	0.15 de	0.030 d	0.45 c
15		0.030 d	0.004 c	0.07 d	0.54 de	0.064 cd	0.074 de	ND d	0.27 c
21		ND d ^d	ND c	ND d	0.074 e	ND d	0.006 e	ND d	ND c
Chinese broccoli									
	MRL	2.0/4	0.5	0.1	2.0/7	0.5/7	0.1	0.1	0.1
0		3.5 a	4.4 a	8.0 a	3.5 a	0.48 a	1.3 a	1.1 a	3.4 a
3		0.25 b	0.12 b	0.61 b	0.80 b	0.17 b	0.32 b	0.059 b	1.1 b
7		0.056 b	0.02 b	0.20 b	0.35 bc	0.089 bc	0.18 b	ND b	0.51 bc
13		ND b	ND b	ND b	0.054 c	ND c	ND b	ND b	ND c
fuzzy squash									
	MRL	0.1	3.0/3	0.1	1.0/2	0.1	0.1	0.1	0.1
0		0.076 a	0.070 a	0.097 a	0.18 a	ND	ND	0.038 a	0.16 a
3		0.035 ab	0.007 b	0.03 b	0.087 a	ND	ND	0.038 a	0.15 a
7		0.011 b	0.002 b	0.01 b	0.079 a	ND	ND	ND b	0.065 a
13		ND b	ND b	ND b	0.049 a	ND	ND	ND b	0.079 a

^a Bok choy treated August 19; mean temperature during study 19.2 °C (15–25 °C); accumulated rainfall 11.8 mm (1–3 mm). Chinese broccoli and fuzzy squash treated August 27; mean temperature during study 19.5 °C (12–26 °C); accumulated rainfall 17.6 mm (1–5 mm). Rate of application (kg of AI/ha) and MRL (mg/kg)/PHI (days, where recommended) indicated below name, beside crop. ^b Mean of four replicates. Endosulfan = endosulfan I + endosulfan II + endosulfan sulfate; pirimicarb = pirimicarb + desmethyl pirimicarb; iprodione = iprodione + RP30228. ^c For each crop, means within a column followed by the same letter are not significantly different ($P \leq 0.05$; LSD test). ^d ND = not detected.

Table 3. Pesticide Residues in Cabbage, Chinese Cabbage, and Bok Choi^a

days after application	rate	residue (mg/kg) ^b for indicated pesticide								
		diazinon	parathion	cypermethrin	captan	carbofuran	metalaxyl	iprodione	mancozeb	endosulfan
	MRL	0.25	0.26	0.07	3.4	0.53	1.0	1.0	2.0	1.1
cabbage										
0		0.13 d ^c	0.14 d	0.050 ef	0.072 e	0.43 de	1.2 d	0.91 ef	1.4 efg	0.78 bcd
1		0.088 d	0.084 d	0.065 def	0.23 e	0.19 e	0.62 d	0.79 ef	0.85 ghij	0.75 bcd
3		0.029 d	0.017 d	0.056 def	0.043 e	0.029 e	0.14 d	0.23 ef	0.68 ghij	0.30 bcd
7		0.010 d	0.004 d	0.024 f	0.040 e	0.011 e	0.061 d	0.14 f	0.41 hij	0.20 bcd
10		0.006 d	ND d	0.14 cdef	0.69 e	ND e ^d	0.036 d	0.055 f	0.33 ij	0.11 bcd
14		0.007 d	0.006 d	0.012 f	ND e	0.29 e	0.048 d	0.065 f	0.22 j	0.055 d
Chinese cabbage										
0		0.97 b	1.1 bc	0.32 b	7.7 bc	3.3 b	7.5 b	6.0 b	5.0 b	4.6 b
1		0.47 c	0.56 c	0.26 bc	6.1 c	0.99 cd	2.4 c	2.6 d	3.5 c	3.3 bcd
3		0.16 d	0.20 d	0.18 cd	1.6 de	0.27 e	1.1 d	1.4 e	2.2 de	1.8 bcd
7		0.070 d	0.096 d	0.088 def	1.8 de	0.070 e	0.31 d	0.63 ef	1.6 efg	0.77 bcd
10		0.044 d	0.054 d	0.031 f	0.010 e	0.026 e	0.12 d	0.32 ef	1.2 fghi	0.14 cd
14		0.016 d	0.024 d	0.020 f	0.14 e	0.061 e	0.073 d	0.088 f	0.45 hij	0.28 bcd
bok choy										
0		1.6 a	1.5 a	0.66 a	16. a	6.8 a	11. a	11. a	11. a	17. a
1		0.62 c	0.69 c	0.32 b	8.8 b	1.3 c	2.5 c	3.9 c	4.4 bc	4.5 bc
3		0.16 d	0.19 d	0.18 cde	3.6 d	0.22 e	0.79 d	1.2 ef	4.1 bc	2.5 bcd
7		0.086 d	0.13 d	0.23 bc	1.4 de	0.10 e	0.37 d	1.0 ef	2.6 d	1.7 bcd
10		0.043 d	0.055 d	0.18 cde	1.2 de	0.069 e	0.062 d	0.32 ef	1.9 def	1.5 bcd
14		0.038 d	0.025 d	0.085 def	0.013 e	0.16 e	0.12 d	0.20 ef	1.2 fghij	0.84 bcd

^a Treated September 7; mean temperature during study 12.8 °C (6–24 °C); accumulated rainfall 9.2 mm (1–8 mm). Rate of application (kg of AI/ha) and MRL (mg/kg)/PHI (days, where recommended) indicated below name. ^b Mean of four replicates. Endosulfan = endosulfan I + endosulfan II + endosulfan sulfate; iprodione = iprodione + RP30228. ^c Means within a column followed by the same letter are not significantly different ($P \leq 0.05$; LSD test). ^d ND = not detected.

internal leaves. Cabras et al. (12) noted that the residue content in the edible leaves of lettuce is strongly affected by the shape of the lettuce when pesticides are applied to foliage. For each pesticide, residues on the three crops were considered together during statistical evaluation (Table 3). From day 3 to day 14, residues of each pesticide were not significantly different

between crops, with the exception of cypermethrin on Chinese cabbage and bok choy, captan on bok choy, iprodione on Chinese cabbage, and mancozeb on Chinese cabbage and bok choy. Residues of diazinon, parathion, carbofuran, metalaxyl, and endosulfan were not significantly different on the three crops from day 3 to day 14. After day 1, with the exception of

Table 4. Pesticide Residues in Snow Peas^a

days after application	residue (mg/kg) ^b for indicated pesticide		
	dimethoate	malathion	mancozeb
	rate	1.7	1.1
MRL	0.5/3	0.5/3	0.1
0	0.82 a ^c	2.4 a	25. a
1	0.37 b	2.4 a	NA ^d
3	0.22 b	0.18 b	4.8 b
7	0.052 b	0.008 b	1.7 bc
10	0.048 b	0.001 b	1.8 bc
14	ND ^e	ND	ND

^a Treated July 21; mean temperature during study 16.3 °C (13–19 °C); accumulated rainfall 79 mm (1–30 mm). Rate of application (kg of AI/ha) and MRL (mg/kg)/PHI (days, where recommended) indicated below name. ^b Mean of four replicates. ^c Means within a column followed by the same letter are not significantly different ($P \leq 0.05$; LSD test). ^d NA = not analyzed. ^e ND = not detected.

cypermethrin and mancozeb, and except on day 1 for captan and iprodione, there were no significant differences in pesticide residues recorded on Chinese cabbage and bok choy. Residue dissipations tended to be better correlated with a curve described by the residue concentration versus the logarithm of time rather than first-order kinetics. Poorer correlations were observed for cabbage compared to the other two crops. Captan had the shortest half-life at 1.7 days, followed by metalaxyl, iprodione, carbofuran, diazinon, and parathion at about 2.5 days; endosulfan at 3.5 days; and cypermethrin and mancozeb at 4.9 days.

Parathion, cypermethrin, and endosulfan are recommended in Ontario (9) for foliar applications to cabbage with MRLs of 0.7, 0.5, and 2 mg/kg and PHIs of 14, 3, and 7 days, respectively. Residues of these three insecticides on the three crops fell below the MRL by the PHI interval. Iprodione is recommended for use on storage cabbage with an MRL of 0.1 mg/kg and a PHI of 7 days. Residues of iprodione did not decline below the MRLs for cabbage and Chinese cabbage until days 10 and 14, respectively. Diazinon and mancozeb have MRLs on cabbage of 0.75 and 7 mg/kg, respectively, although they are not recommended in Ontario for use on this crop. For the three crops, residues of the two pesticides declined below this MRL by day 1. Braun et al. (7) reported that residues of diazinon and parathion, applied to Chinese cabbage at twice the rate applied in this study, fell below the MRL by days 3 and 7, respectively.

The initial residue deposits of three pesticides on snow peas (**Table 4**) did not correlate with the application rate. First-order kinetics suggested half-lives of 0.85 days for malathion, 2.4 days for dimethoate, and 2.6 days for mancozeb. The residue concentration versus logarithm of time regression showed higher correlations for dimethoate and mancozeb compared to first-order kinetics. Residues of dimethoate and malathion were below 0.1 mg/kg on day 7 and could not be detected by day 14. On day 14, mancozeb was not detected. Dimethoate and malathion are recommended for use in Ontario (9) on peas with an MRL of 0.5 mg/kg and a PHI of 3 days. By days 1 and 3, respectively, residues of dimethoate and malathion on snow peas fell below the MRL for peas.

On Chinese broccoli, the initial residue deposit correlated with application rate (**Table 5**). The two pyrethroid insecticides showed almost identical residue dissipation. First-order kinetics described the residue dissipation with calculated half-lives of 2.0 days for diazinon and 2.5 days for permethrin and cypermethrin. Permethrin and cypermethrin are recommended in Ontario (9) for application on broccoli with an MRL of

Table 5. Pesticide Residues on Chinese Broccoli^a

days after application	residue (mg/kg) ^b for indicated pesticide		
	diazinon	permethrin	cypermethrin
	rate	0.75	0.07
MRL	0.75	0.5/7	0.5/3
0	4.1 a ^c	0.84 a	0.74 b
1	1.5 bc	0.51 b	0.52 c
3	2.4 b	1.2 a	1.0 a
8	0.15 c	0.11 c	0.12 d
10	0.12 c	0.12 c	0.061 d
14	0.021 c	0.009 c	0.013 d

^a Treated August 30; mean temperature during study 16.2 °C (11–23 °C); accumulated rainfall 57.3 mm (1–30 mm). Rate of application (kg of AI/ha) and MRL (mg/kg)/PHI (days, where recommended) indicated below name. ^b Mean of four replicates. ^c Means within a column followed by the same letter are not significantly different ($P \leq 0.05$; LSD test).

0.5 mg/kg and PHIs of 7 and 3 days, respectively. Unfortunately, all residues for day 3 appear anomalously high. By day 8, residues of permethrin and cypermethrin were below the MRL of 0.5 mg/kg for broccoli. Diazinon is not recommended for use in Ontario on broccoli but has an MRL of 0.75 mg/kg. On day 8, the residue of diazinon was below this MRL. The residues were below 0.1 mg/kg on day 10 for cypermethrin and on day 14 for diazinon and permethrin.

In the comparison of residue deposit and dissipation of nine pesticides on lettuce and cabbage cultivars, there were significant differences among the residues determined on the different lettuce cultivars and kale (**Table 6**) for each of the pesticides on day 1 after application. Residues on head lettuce were significantly lower than those on the other cultivars on day 1 for all pesticides except for captan on romaine lettuce. Comparing days 3 and 8, there were no significant differences for residues on the different cultivars for carbofuran, metalaxyl, diazinon, parathion, and iprodione. On day 3, residues on head lettuce were significantly lower than those on the other cultivars with cypermethrin and with mancozeb except for romaine lettuce; residues of endosulfan were higher on leaf and buttercrunch, and captan was higher only on leaf. By day 8, residues were not significantly lower on head lettuce than on other cultivars, except for cypermethrin on endive; mancozeb on romaine, leaf, and endive; and captan on endive. Ripley et al. (25) reported initial deposits of cypermethrin in the order head lettuce < romaine < endive, but after 7–14 days, the concentrations were about the same on the three types of lettuce.

The Ontario recommendations (9) for pesticide foliar applications on lettuce and endive are as follows: for diazinon, cypermethrin, endosulfan, iprodione and metalaxyl plus mancozeb, the MRLs are 0.75, 0.1, 2, 15, 5, and 7 mg/kg and the PHIs are 10, 14, 14, 4, 14, and 14 days, respectively; for parathion on lettuce and leaf lettuce, the MRL is 0.7 mg/kg and the PHIs are 7 and 21 days, respectively. Residues of diazinon, parathion, iprodione, and metalaxyl on the five lettuce cultivars fell below the MRLs by days 1, 3, 3, and 3, respectively. Only head and romaine lettuce were below the MRL by day 8 for endosulfan, and head and buttercrunch lettuce by day 8 for mancozeb. By day 8, cypermethrin residues had not fallen below the MRL for any tested lettuce cultivar.

Residues of the different pesticides on lettuce and kale on day 1 (**Table 6**) generally reflected the application rate, with exception of the two organophosphorus insecticides. Higher residues occurred with captan, endosulfan, iprodione, metalaxyl, and mancozeb, whereas the lowest occurred with cypermethrin. Diazinon and parathion residues were lower than the rate of

Table 6. Pesticide Residues on Lettuce Cultivars and Kale 1, 3, and 8 Days after Application^a

cultivar	rate MRL	residue (mg/kg) ^b for indicated pesticide								
		cypermethrin	captan	carbofuran	metalaxyl	diazinon	parathion	mancozeb	endosulfan	iprodione
		0.07	3.4	0.53	1.0	0.25	0.26	2.0	1.1	1.0
		0.1/14	0.1	0.1	5.0/14	0.75/10	0.7/7,21	7.0/14	2.0/14	15/4
1 day after application										
head		0.36 efg ^c	11. cd	1.5 d	4.1 d	0.19 c	0.42 c	12. def	4.4 def	5.8 e
romaine		0.78 bc	8.9 cde	3.0 c	9.0 c	0.37 b	0.83 b	18. c	10. c	13. d
leaf		1.4 a	27. a	8.6 a	17. a	0.64 a	1.4 a	33. a	22. a	28. a
endive		1.4 a	24. a	5.5 b	14. b	0.58 a	1.3 a	34. a	17. b	18. c
buttercrunch		0.9 b	23. ab	4.8 b	9.9 c	0.58 a	0.92 b	28. b	17. b	15. cd
kale ^d		1.6 a	22. ab	8.1 a	17. a	0.52 a	0.92 b	28. b	21. a	23. b
3 days after application										
head		0.21 g	1.7 e	0.40 de	0.095 e	0.013 d	0.017 d	4.4 h	0.74 g	0.17 f
romaine		0.52 def	2.4 e	0.18 de	1.0 e	0.074 cd	0.17 cd	9.2 fgh	2.8 defg	1.3 f
leaf		0.71 bcd	15. bc	0.19 de	0.74 e	0.099 cd	0.21 cd	15. cde	4.6 def	1.3 f
endive		0.77 bc	8.7 cde	0.38 de	1.6 e	0.078 cd	0.12 d	13. def	3.8 defg	1.5 f
buttercrunch		0.59 cde	9.7 cde	0.25 de	1.0 e	0.10 cd	0.23 cd	11. efg	4.8 de	1.6 ef
kale ^d		0.70 bcd	1.8 e	0.20 de	1.0 e	0.12 cd	0.12 d	16. cd	3.7 defg	1.0 f
8 days after application										
head		0.19 g	2.3 e	0.027 e	0.21 e	0.009 d	0.018 d	4.4 h	0.70 g	0.70 f
romaine		0.34 efg	4.1 de	0.045 e	0.50 e	0.033 d	0.050 d	11. defg	1.5 efg	2.2 ef
leaf		0.41 efg	9.9 cde	0.076 de	0.47 e	0.024 d	0.070 d	10. efg	2.2 efg	1.9 ef
endive		0.71 bcd	11. cd	0.12 de	1.0 e	0.049 d	0.089 d	10. efg	3.0 defg	1.5 f
buttercrunch		0.31 fg	8.7 cde	0.088 de	0.54 e	0.025 d	0.071 d	6.6 gh	2.2 efg	1.7 ef
kale ^d		0.30 fg	1.2 e	0.044 e	0.41 e	0.019 d	0.012 d	8.3 fgh	1.4 efg	0.86 f

^a Treated August 29; mean temperature during study 13.7 °C (11–17 °C); accumulated rainfall 15 mm (4–11 mm). Rate of application (kg of AI/ha) and MRL (mg/kg)/PHI (days, where recommended) indicated below name. ^b Mean of four replicates. Endosulfan = endosulfan I + endosulfan II + endosulfan sulfate; iprodione = iprodione + RP30228. ^c Means within a column followed by the same letter are not significantly different ($P \leq 0.05$; LSD test). ^d See **Table 7** for MRL and PHI for kale.

application might suggest, relative to the other pesticides. Previous studies (7, 15, 26) have consistently shown a dramatic initial decline in organophosphorus insecticide residues on plant foliage during the first 48 h after application. Between day 1 and day 8, residues of carbofuran, diazinon, parathion, and metalaxyl decreased from 90 to 99%, whereas captan, cypermethrin, and mancozeb declined more slowly with about 40–80% dissipation. The declines of endosulfan and iprodione were intermediate with about 83–96% loss during the study period. The percent of day 8 relative to day 1 residue was generally highest on romaine, endive, head, and buttercrunch and lowest on leaf and kale.

In the trial with cabbage cultivars (**Table 7**), the residue concentration for the individual pesticides on cabbage, savoy cabbage, Chinese cabbage, and tah tsai was not significantly different on the four crops from day 1 to day 7, except for metalaxyl on day 1 on savoy cabbage and Chinese cabbage, diazinon on savoy cabbage on day 1, and carbofuran on day 7 on Chinese cabbage. Bok choy and often mei quing choy showed significantly higher residue concentrations than the other cultivars. Bok choy was significantly different from all other cultivars for each pesticide on day 1. On day 3, residues on bok choy were significantly higher than those on the other cultivars with all pesticides except captan, as well as savoy cabbage with diazinon and mei quing choy with cypermethrin, diazinon, parathion, mancozeb, endosulfan, and iprodione. By day 7, residues on bok choy were significantly higher compared to other cultivars for only carbofuran and metalaxyl; residues of cypermethrin and iprodione were higher on mei quing choy than on bok choy. Overall, the residues were quite variable, with the mean concentration being similar for the 3 days studied on all varieties, except for bok choy and mei quing choy, which showed dissipation over time. The highest residues were determined on bok choy and mei quing choy, whereas cabbage, savoy cabbage, and tah tsai generally had the lowest.

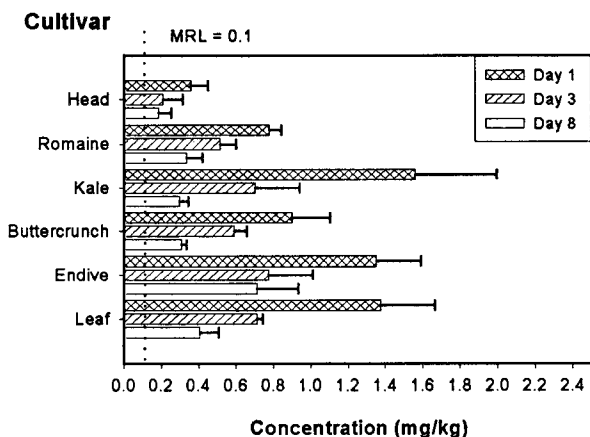
Cypermethrin, endosulfan, and parathion are recommended in Ontario for foliar application on cabbage with MRLs of 0.5, 2, and 0.7 mg/kg and PHIs of 3, 7, and 14 days, respectively. Residues of these three pesticides on the six cultivars fell below the MRLs by the indicated PHIs, except for endosulfan on bok choy and mei quing choy. Diazinon, mancozeb, and metalaxyl have MRLs on cabbage of 0.75, 7, and 2 mg/kg, respectively. Residues on all six cultivars fell below the MRLs for diazinon and metalaxyl by day 1 and for mancozeb by day 7.

For the lettuce cultivars and kale (**Table 6**), residues of the nine pesticides on each of the six crops at day 1 correlated well ($R^2 > 0.94$) with the application rate, except for captan, residues of which appeared to be about 50% less than predicted. Residues of iprodione were slightly higher than those of metalaxyl although both were applied at the same rate. Cypermethrin residues also were higher than suggested by the regression equation. Similar trends were evident for the cabbage cultivars (**Table 7**), although lower regression coefficients were determined. With the same tank mix and rate of application, residues on the cabbage cultivars were considerably lower than those on lettuce, perhaps because less pesticide adheres to the waxier cabbage leaves. On the cabbage cultivars, the highest residues on day 1, observed on bok choy and mei quing choy, were comparable to the levels on head lettuce, which had the lowest residues of all lettuce varieties examined. In general, the highest residues on day 1 on cabbage cultivars fell in the order mancozeb > endosulfan > captan > iprodione. Lower residue concentrations on day 1 were observed with carbofuran and metalaxyl, whereas the cypermethrin concentrations were comparable to those of diazinon and parathion. The captan, diazinon, and parathion concentrations decreased by >80% over the 7 days on bok choy, whereas endosulfan, cypermethrin, iprodione, and mancozeb decreased by 55–80%; the carbofuran concentrations did not decline. Smaller losses were observed with mei quing choy.

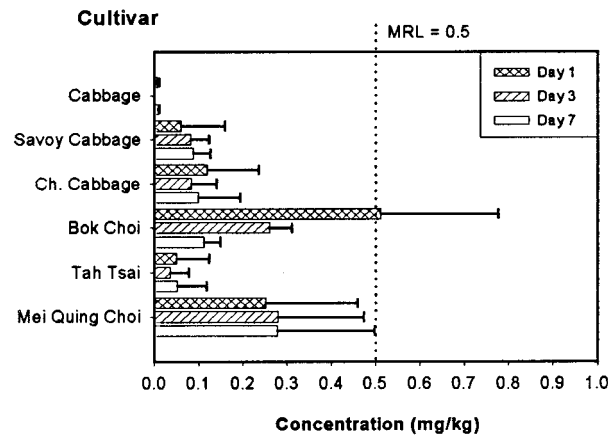
Table 7. Pesticide Residues on Cabbage Cultivars 1, 3, and 7 Days after Application^a

cultivar	residue (mg/kg) ^b for indicated pesticide									
	rate	cypermethrin	captan	carbofuran	metalaxyl	diazinon	parathion	mancozeb	endosulfan	iprodione
	MRL	0.07	3.4	0.53	1.0	0.25	0.26	2.0	1.1	1.0
		0.5/3	0.1	0.1	2.0	0.75	0.7/14	7.0	2.0/7	0.1
1 day after application										
cabbage		0.007 f ^c	0.025 c	0.017 d	0.037 de	0.013 ef	0.010 d	1.1 fg	0.12 d	0.076 ef
savoy cabbage		0.060 f	0.032 c	0.32 bcd	0.55 cd	0.16 bcde	0.20 bcd	2.1 efg	0.94 cd	0.82 cdef
Chinese cabbage		0.12 cdef	0.49 bc	0.24 bcd	0.56 c	0.078 bcdef	0.12 cd	1.5 fg	0.91 cd	0.52 def
bok choi		0.51 a	13. a	1.0 a	1.9 a	0.50 a	0.71 a	10. a	5.7 a	4.6 a
tah tsai		0.050 f	0.32 bc	0.06 cd	0.13 cde	0.049 cdef	0.054 cd	1.2 fg	0.75 d	0.25 ef
mei quing choi		0.25 bcde	2.5 bc	0.24 bcd	0.51 cde	0.18 bcd	0.26 bc	6.0 bc	2.8 b	1.7 bcd
3 days after application										
cabbage		ND ^d f	ND c	ND d	0.004 e	0.004 f	ND d	0.35 g	0.008 d	0.011 f
savoy cabbage		0.062 f	ND c	0.12 cd	0.18 cde	0.073 bcdef	0.093 cd	2.0 efg	0.63 d	0.31 def
Chinese cabbage		0.083 f	0.30 bc	0.28 bcd	0.34 cde	0.040 def	0.098 cd	1.7 fg	0.74 d	0.57 def
bok choi		0.26 bcd	1.3 bc	0.98 a	1.1 b	0.20 b	0.35 b	5.7 bcd	2.9 b	2.0 bc
tah tsai		0.027 f	0.15 c	0.026 cd	0.026 de	0.017 ef	0.017 d	1.7 efg	0.32 d	0.096 ef
mei quing choi		0.28 b	5.1 b	0.40 bc	0.54 cd	0.19 bc	0.36 b	7.7 b	3.2 b	2.5 b
7 days after application										
cabbage		0.005 f	0.016 c	0.022 cd	0.034 de	0.013 ef	0.004 d	0.45 g	0.042 d	0.10 ef
savoy cabbage		0.088 f	ND c	0.29 bcd	0.38 cde	0.072 bcdef	0.067 cd	2.5 efg	1.0 cd	0.43 def
Chinese cabbage		0.098 ef	1.1 bc	0.51 b	0.49 cde	0.070 bcdef	0.13 cd	2.5 efg	1.1 cd	0.88 cdef
bok choi		0.11 def	1.7 bc	1.1 a	1.2 b	0.089 bcdef	0.11 cd	3.4 def	2.5 bc	1.4 bcdef
tah tsai		0.051 f	0.12 c	0.049 cd	0.057 cde	0.037 ef	0.054 cd	1.0 g	0.87 cd	0.23 ef
mei quing choi		0.28 bc	4.4 bc	0.23 bcd	0.36 cde	0.084 bcdef	0.11 cde	4.0 cde	3.6 b	1.5 a

^aTreated September 26; mean temperature during study 12 °C (5–22 °C); accumulated rainfall 5.4 mm (1–4.4 mm). Rate of application (kg of AI/ha) and MRL (mg/kg)/PHI (days, where recommended) indicated below name. ^bMean of four replicates. Endosulfan = endosulfan I + endosulfan II + endosulfan sulfate; iprodione = iprodione + RP30228. ^cMeans within a column followed by the same letter are not significantly different ($P \leq 0.05$; LSD test). ^dND = not detected.

**Figure 1.** Cypermethrin residues on lettuce cultivars and kale on days 1, 3, and 8 after application.

Lower residues were observed on the storage cabbage because of its larger mass-to-surface area ratio. The residue level was also lower on those cultivars, such as cabbage and head lettuce, where the external leaves cover the internal leaves, protecting them from the pesticide deposits. Higher residues were observed with the cabbage cultivars bok choi and mei quing choi and with the lettuce cultivars endive, leaf, and buttercrunch, where the head is more open-shaped and the external leaves do not cover the internal leaves, thereby allowing pesticide to deposit on all leaves. Cabras et al. (12) showed that the residue content was heavily affected by the lettuce structure; cos lettuce had very high residues on edible leaves at application time, whereas residues were lower on crisphead lettuce because the external leaves completely covered the internal ones, protecting them from contamination. Pesticide application on head lettuce was simulated by Sances et al. (13) to determine the amount and location of pesticide residue within lettuce heads at harvest and to determine whether wrapper leaf removal reduces residues

**Figure 2.** Cypermethrin residues on cabbage cultivars on days 1, 3, and 7 after application.

on the marketable head. For all materials studied, they reported that removal of the wrapper leaf resulted in a low-residue or residue-free head of lettuce. In this study, wrapper leaves were not removed; head lettuce had the lowest residue because fewer leaves were exposed to the pesticides and also because the mass-to-surface area ratio was higher, which diluted the overall residue concentration.

The relative residues of cypermethrin on the lettuce and cabbage cultivars are illustrated in **Figures 1 and 2**, respectively. The lowest residues were observed with the round, tightly wrapped heads of lettuce and cabbage, where the small surface area-to-mass ratio effectively diluted the residue concentration. In contrast, the highest residues were observed on open, leafy types, where more residue was deposited on all leaves rather than only on the outside, wrapper leaves. Different preharvest intervals will be necessary to achieve MRLs of 0.1 mg/kg for lettuce and 0.5 mg/kg for cabbage. Even after 8 days, residues of cypermethrin exceeded 0.1 mg/kg on all lettuce types.

In conclusion, with lettuce and cabbage cultivars, structure significantly affects pesticide deposit and dissipation. It is evident that different PHIs are necessary to achieve established MRLs for the different cultivars. These results clearly indicate the need to examine residue dissipation on individual groups of specialty crops and to establish individual MRLs when significant differences in residues are observed. Therefore, to avoid violations of the MRLs, the pesticide recommendations for major vegetable crops should not be extended to minor crops without investigation of the necessary changes in the preharvest intervals.

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