Distribution of Insecticide Residues in Carrots at Harvest

Douglas G. Finlayson,* Ian H. Williams, Marilyn J. Brown, and Colin J. Campbell

Carrots grown in muck soil and treated with the insecticides carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate), ethion (*O,O,O',O'*-tetraethyl *S,S'*-methylene bisphosphorodithioate), fensulfothion (*O,O*-diethyl *O-p*-[(methylsulfinyl)phenyl] phosphorothioate), and phorate (*O,O*-diethyl *S*-[(ethylthio)methyl] phosphorodithioate), were sectioned, halved longitudinally, and peeled and the insecticide residues determined for whole carrots, sections of carrots, peel, and pulp. Residues for all insecticides were greater in the peel than in the pulp, and greater in the top portion of the carrot than in the lower sections. More than 50% of the residues of ethion, fensulfothion, and phorate were located in the top 0–3 cm of the carrot. Carbofuran residues in the same section were slightly less. Residue levels generally increased with higher rates and numbers of applications. Total residues in whole carrots ranged from 0.06 ppm for ethion at the lowest rate to 0.49 ppm for fensulfothion at the highest rate.

When strains of the carrot rust fly, *Psila rosae* (Fab.), became resistant to organochlorine insecticides, experiments were conducted to determine the methods and rates of application for substitute insecticides which would prevent damage by the rust fly maggot. In the United Kingdom, Wheatley (1971) and in Canada, Finlayson et al. (1966, 1972) showed that damage from carrot maggots could be prevented by preseeding applications of pesticides to the soil, by postemergence applications to the foliage, or by combinations of the two. Regardless of the methods or rates of application, residues of the insecticides were present in the carrots at harvest.

In this experiment we investigated the four insecticides most effective in preventing damage by carrot maggots while leaving low levels of residues. The compounds were: carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate), ethion (*O,O,O',O'*-tetraethyl *S,S'*-methylene bisphosphorodithioate), and fensulfothion (*O,O*-diethyl *O-p*-[(methylsulfinyl)phenyl] phosphorothioate) (Finlayson et al. 1972), and phorate (*O,O*-diethyl *S*-[(ethylthio)methyl] phosphorodithioate) which is recommended for carrot rust fly control in the United Kingdom (Ministry of Agriculture, Fisheries and Food, 1972).

The purpose of the experiment was to compare residue levels using different rates and methods of application of the insecticides and to determine the distribution of their residues within the carrot.

MATERIALS AND METHODS

Carrot Growing and Application of Insecticides. At two locations in muck soil carrots (C.V. Gold Pak) were seeded early and late in four-row raised beds. Ten carrots were taken from each replicate for residue analyses 30 days after the final spray.

Early-seeded carrots were sown in early April with a four-row Planet Jr. seeder. Sprays of carbofuran, ethion, fensulfothion, and phorate were applied when the carrot seedlings were in the forked-leaf stage, at 16 oz of toxicant in 100 gal of water/acre. Supplementary sprays at the same rate were applied 20, 40, and 60 days later (four sprays). Sprays at the same rate were applied to a second section in the forked-leaf stage and again 30 and 60 days later (three sprays).

Late-seeded carrots were sown June 23 in four-row raised beds with a rod-row, V-belt seeder. Granular insecticides at 0.5 and 1.0 oz of toxicant/1000 ft of row were applied with the seed. The seed and the insecticide granules were separated on the belt by a fine layer of soil over the seed. The seeder was equipped with a scatter-shoe so that the seed and the insecticide were distributed in a 2-in. band. The applications of granules were followed by supplementary sprays at 16 oz of toxicant in 100 gal of water/acre per application. Two schedules of sprays were applied: at 30, 50, and 70 days after seeding (three sprays), and at 40 and 70 days after seeding (two sprays).

Residue Analysis. The carrots were scrubbed to remove soil particles, and the top of the carrot was pared with a knife to remove any stems from the root–stem interface. Twenty-four carrots per treatment, six from each replicate, were sectioned from top to bottom of the carrot as follows: top section, 0–3 cm; upper section, 3–6 cm; middle section and the bottom section comprising the lowest 8 cm. Each section was halved longitudinally and then one-half was peeled. There were thus three samples per section: peel, pulp, and the whole.

The remaining 16 carrots, 4 per replicate, were stored for analysis as whole roots. All samples were placed in frozen storage immediately after the preparations were completed.

When residues in the carrots were to be determined the frozen samples were shredded in a Braun Multimix, tumbled, sub-sampled to 50 g, and treated as follows. Carbofuran was extracted by the method of Cook et al. (1969) as modified by Williams and Brown (1973). Determination was by gas chromatography with nitrogen detection using a Coulson conductivity detector. Ethion was extracted with ethyl acetate by the method of Watts and Storherr (1965), sweep co-distilled by the method of Storherr and Watts (1965), and determined by gas chromatography using a flame photometric detector. Fensulfothion was determined by the method of Williams et al. (1971). Phorate was determined by the method of Suett (1971) as modified by Brown (1975).

RESULTS AND DISCUSSION

Residues of the insecticides and their primary metabolites are presented in tabular form. Since the amount of residue is almost directly proportional to the total rate of the insecticide applied, the only detailed data presented are from the lowest rate, three sprays at 1 lb of toxicant/application to early-seeded carrots (Table I), and from the highest rate where 1 oz of toxicant/1000 ft of row was applied at seeding of late carrots followed by three sprays as above (Table II). Residue totals from the other four schedules of treatments together with totals from Tables I and II are shown in Table III.

Carbofuran (C) and 3-Hydroxycarbofuran (3-OH). Little or none of the parent compound was recovered. Of

Research Station, Agriculture Canada, Vancouver, British Columbia, Canada V6T 1X2.

Table I. Residues of Insecticides and Their Primary Metabolites in Early-Seeded Carrots Sprayed 30, 50, and 70 Days after Seeding[a]

	Carbofuran			Fensulfothion		Phorate		
Carrot section	C	3-OH	Ethion	F	FSO_2	P	PSO	PSO_2
Whole root	t	0.18	0.06	0.22	0.07	0.01	0.07	0.10
Top, 0-3 cm								
Peel	t	0.38	1.25	1.08	0.65	0.05	1.76	1.29
Pulp	nd	0.12	0.05	0.23	0.05	0.01	0.15	0.14
Whole	nd	0.32	0.21	0.29	0.11	0.02	0.19	0.15
Upper, 3-6 cm								
Peel	nd	0.61	0.17	0.61	0.38	t	0.22	0.51
Pulp	nd	0.14	nd	0.04	0.02	nd	0.04	0.05
Whole	nd	0.11	0.03	0.05	0.04	nd	0.06	0.10
Middle								
Peel	t	0.28	0.05	0.22	0.11	t	nd	0.10
Pulp	nd	0.08	nd	0.02	nd	nd	nd	0.02
Whole	nd	0.09	nd	0.03	0.02	nd	nd	0.03
Bottom, 8 cm								
Peel	t	0.15	0.03	0.38	0.07	nd	0.02	0.11
Pulp	t	0.11	t	0.01	t	nd	nd	nd
Whole	nd	0.06	nd	0.01	0.01	nd	nd	0.01

[a] t = trace, <0.02 for carbofuran and ethion and <0.01 for fensulfothion and phorate. nd = none detectable.

Table II. Residues of Insecticides and Their Primary Metabolites in Late-Seeded Carrots Treated at Seeding and Sprayed 30, 50, and 70 Days Later[a]

	Carbofuran			Fensulfothion		Phorate		
Carrot section	C	3-OH	Ethion	F	FSO_2	P	PSO	PSO_2
Whole root	t	0.29	0.12	0.28	0.21	0.02	0.24	0.14
Top, 0-3 cm								
Peel	0.02	1.12	4.19	4.13	1.77	0.18	5.70	1.26
Pulp	nd	0.32	0.07	0.18	0.07	0.02	0.17	0.16
Whole	t	0.40	0.66	0.68	0.37	nd	0.62	0.42
Upper, 3-6 cm								
Peel	0.05	0.63	0.60	1.25	0.62	nd	0.48	0.53
Pulp	0.02	0.21	t	0.06	0.01	nd	0.05	0.08
Whole	nd	0.19	0.07	0.12	0.09	nd	0.06	0.12
Middle								
Peel	0.04	0.22	0.08	0.54	0.29	nd	0.16	0.20
Pulp	nd	0.10	t	0.02	0.01	nd	t	t
Whole	t	0.14	0.02	0.07	0.02	nd	nd	0.04
Bottom, 8 cm								
Peel	0.04	0.16	0.03	0.11	0.06	nd	0.04	0.06
Pulp	nd	0.06	t	0.02	0.01	nd	t	t
Whole	t	0.11	t	0.03	0.02	nd	nd	0.02

[a] t = trace, <0.02 for carbofuran and ethion and <0.01 for fensulfothion and phorate. nd = none detectable.

the 78 analyses only 10 had measurable amounts of carbofuran ranging from 0.02 to 0.11 ppm. In general, most of the insecticide and its metabolite occurred in the peel of the top 3 cm of the carrot. As the total amount applied increased so also did the residue.

Ethion. The residues were similar in amounts to those of carbofuran and its metabolite for the whole carrot, but were from 3 to 4 times higher in the top 3 cm. Again, the peel contained most of the insecticide, ranging from 1.25 ppm at the lowest to 4.19 at the highest rate of application. In contrast to carrots treated with carbofuran, residues in the pulp were almost negligible. Residues in the peel from the botton 8 cm of the carrot ranged from 0.02 to 0.09 ppm.

Fensulfothion (F) and Fensulfothion Sulfone (FSO_2). Residues from the whole carrot ranged from 0.14 to 0.49 ppm. Finlayson et al. (1972) found a range of 0.31 to 0.45 ppm in whole carrots 30 days after the final application. However, when the distribution of the insecticide in the carrot was investigated, its pattern was similar to that of carbofuran but, like ethion, the amounts were some 4 times greater in the top 3 cm, where the peel had a total pesticide load that ranged from 1.02 to 7.70 ppm. Although there was much less in the pulp, measurable amounts were recorded from all sections. Chisholm (1974) reported about 0.10 ppm of the sulfone in carrots grown in soil treated the previous year at 5.6 kg of active ingredient/ha for rutabaga.

Table III. Total Residues in Parts per Million (Parent Compound and Metabolites) in Early- and Late-Seeded Carrots 30 Days after the Final Application of Several Schedules of Treatments[a]

	Early carrots		Late carrots 0.5 oz		Late carrots 1.0 oz	
Insecticide	3 sprays	4 sprays	2 sprays	3 sprays	2 sprays	3 sprays
Carbofuran	0.18	0.24	0.12	0.25	0.24	0.29
Ethion	0.06	0.12	0.19	0.22	0.23	0.12
Fensulfothion	0.29	0.14	0.37	0.48	0.36	0.49
Phorate	0.18	0.19	0.18	0.19	0.26	0.40

[a] Treatment schedules: early carrots, no soil treatment, 3 or 4 sprays at 1.0 lb of active ingredient/acre per application; late carrots, 0.5 or 1.0 oz of active ingredient/1000 ft of row incorporated at seeding followed by 2 or 3 sprays at 1.0 lb of active ingredient/acre per application.

Phorate (P), Phorate Sulfoxide (PSO), and Phorate Sulfone (PSO_2). Only the phorate sulfoxide and sulfone metabolites are included. The oxygen analogue of phorate was included in the analysis, but the amounts recovered never exceeded 0.12 ppm; about 70% of the samples had only a trace or none. Total residues for the whole carrot ranged from 0.18 to 0.40 ppm. The residues were greater in the peel than in the pulp by a factor of approximately 10:1. Total residues in the top 3-cm section ranged from 0.33 to 1.47 ppm; in the upper 3–6 cm section residues were much less and ranged from 0.04 to 0.25. In the middle and bottom sections maximum residues were 0.13 and 0.05 ppm, respectively. Total residue levels for whole carrots did not differ appreciably for the four insecticides investigated (Table III). However, there was considerable variation in their distribution within the carrot, which may have some bearing on the efficacy of the insecticides for preventing carrot maggot damage.

Wheatley and Hardman (1967) suggested that larval toxicity results from translocation of the insecticides through the lateral roots to the lateral feeding sites, so that control is achieved by feeding rather than by contact action against eggs and larvae. Finlayson and Suett (1975) suggested that insecticide residues in the soil contribute more to the late protection of carrots from carrot maggot than do residues within the carrot because those within the carrot are diluted by growth. This study indicates that other factors may also be involved, for instance, the concentration of residues in the upper peel and the near absence of residues in the lower level of the root. Ethion was concentrated mostly in the peel and in the upper sections of the carrots which were well protected. But the roots were damaged more severely in the lower half than were carrots treated with carbofuran or fensulfothion (Finlayson et al., 1972). These treatments resulted in residues more than twice as high in the bottom 8 cm than those resulting from ethion treatment. The proportion of the total residue levels within the top 3 cm was calculated; for three of the insecticides more than 50% was present. Carbofuran residues in the same section were slightly more than 40%. This difference in distribution may be attributed to the greater water solubility of carbofuran allowing deeper penetration of the aqueous sprays in the soil. It is thus evident that the common practice of discarding the top 0.5 in. of the carrot and peeling the rest removes most of the residue.

LITERATURE CITED

Brown, M. J., *J. Agric. Food Chem.* **23**, 334 (1975).
Chisholm, D., *Can. J. Plant Sci.* **54**, 667 (1974).
Cook, R. F., Stanovick, R. P., Cassil, C. C., *J. Agric. Food Chem.* **17**, 277 (1969).
Finlayson, D. G., Brown, M. J., Campbell, C. J., Williams, I. H., *J. Entomol. Soc. B.C.* **69**, 14 (1972).
Finlayson, D. G., Fulton, H. G., Noble, M. D., *J. Econ. Entomol.* **59**, 1082 (1966).
Finlayson, D. G., Suett, D. L., *J. Econ. Entomol.* **68**, 140 (1975).
Ministry of Agriculture, Fisheries and Food, "Agricultural Chemicals Approval Scheme", 1972, 168 pp.
Storherr, R. W., Watts, R. R., *J. Assoc. Off. Agric. Chem.* **48**, 1154 (1965).
Suett, D. L., *Pestic. Sci.* **2**, 105 (1971).
Watts, R. R., Storherr, R. W., *J. Assoc. Off. Agric. Chem.* **48**, 1158 (1965).
Wheatley, G. A., *Proc. Br. Insectic. Fungic. Conf., 6th*, 386 (1971).
Wheatley, G. A., Hardman, J., *Rep. Nat. Veg. Res. Stn. 1966*, 63 (1967).
Williams, I. H., Brown, M. J., *J. Agric. Food Chem.* 21, 399 (1973).
Williams, I. H., Kore, R., Finlayson, D. G., *J. Agric. Food Chem.* **19**, 456 (1971).

Received for review November 3, 1975. Accepted January 28, 1976.

Degradation of Endosulfan and Ethion on Pears and Pear and Grape Foliage

James D. MacNeil* and Mitsuru Hikichi

A mixture of endosulfan (6 lb of Thiodan-50 WP) and ethion (8 lb of Ethion-25 WP) recommended for control of pear psylla was applied to four experimental blocks of pear trees to study rates of degradation. In addition, two blocks of pears were treated with endosulfan (6 lb of Thiodan-50 WP) only and two blocks were treated with the endosulfan–ethion mixture to determine insecticide residues at harvest. Endosulfan residues on treated fruit were below the 2 ppm tolerance established for endosulfan on pears 14 days after application. Ethion residues were within the 1 ppm tolerance 20–35 days after application. Degradation rates of the two insecticides on pear and grape foliage are also reported.

Pear psylla (*Psylla pyricola* Foerster) is a major pest of pear orchards, causing discoloration and damage to both fruit and leaves. A major problem in controlling this insect is its rapid development of resistance to control materials. Present recommendations for summer control include endosulfan alone or in combination with ethion.

Endosulfan (6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methane-2,4,3-benzodioxathiepine 3-oxide) occurs in technical mixtures as two isomers, usually designated α and β in an approximate ratio of 70:30. The chemistry of endosulfan has been reviewed by Maier-Bode (1968). The only investigations he reported of residues of endosulfan on pears were those done by Cassil (1960) in California. Samples analyzed 1 and 3 weeks after final application of the insecticide (following applications in May, July, and August with a total of 3.5 lb of active ingredient per acre), showed total residues of α- and β-endosulfan to be 0.2 ppm 3 weeks after the August application.

Ethion, tetraethyl S,S^1-methylene bis(phosphorothiolethionate), is a nonsystemic insecticide and acaricide that is registered for control of a variety of fruit insects in Canada. The persistence of ethion in soil, water-borne silt, crops, and the atmosphere was studied by Hinden and Bennett (1970), who found no carryover of residues of ethion in soil from year to year and residues in crops at

Research Station, Agriculture Canada, Summerland, British Columbia, VOH IZO, Canada.