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Residues of Insecticides, Fungicides, and Herbicides in Fruit Produced in Ontario, Canada, 1980–1984

R. Frank, H. E. Braun, and B. D. Ripley

Provincial Pesticide Residue Testing Laboratory, Agricultural Laboratory Services Branch, Ontario Ministry of Agriculture and Food, % University of Guelph, Guelph, Ontario N1G 2W1, Canada

A wide range of pesticides are registered by the Federal Government and recommended by the Provincial Government for the production of fruit in Ontario, Canada. Health & Welfare Canada (Anonymous 1985) have established maximum residue limits (MRL) for most compounds on most commodities. Where no MRL is specified in the Act and Regulations, a negligible limit (<0.1 mg/kg) is applied.

Increased public awareness and concern about the use of pesticides and chemicals in general, their residues in food and the environment, and their toxic effects has increased the demands to detect and measure these residues at trace concentrations. Some of the monitoring is conducted by the Federal Government for regulatory purposes whereas the Provincial Government ensures that the Provincial recommendations on the use of pesticides do not result in crops that contain residues in violation of the MRL.

This paper is a report of the monitoring of three fruit commodities (sweet cherries, peaches and strawberries), domestically produced within the Province of Ontario. Table 1 shows the number of different pesticidal groups that were registered and recommended to fruit growers from 1980 to 1984 (Anonymous 1980-84). The analysis program was undertaken to monitor most of the insecticides and the major fungicides, especially those used late in the season and close to harvest (Table 2). Some pesticides were sought that were not registered or recommended; the chlorophenoxy and chlorobenzoic acid herbicides were included because of complaints of spray drift from grain crops to fruit crops.

MATERIAL AND METHODS

Composite samples of cherries, peaches and strawberries were sampled upon delivery to farmer's wholesale markets at Leamington and Toronto, Ontario. In addition, samples of strawberries were collected from farms with pick-your-own operations in the Norfolk County area in southwestern Ontario and from growers in the Georgian Bay area of western Ontario. Composite samples consisted of 0.5 kg of cherries and strawberries and 10 to 15 peach fruit. Samples were shipped to the laboratory within two days of collection and analyses were commenced within two days of receipt. In the laboratory, samples were refrigerated until analyzed.

Table 1. Number of pesticides registered and recommended in the Province of Ontario between 1980 and 1984 on the three fruit commodities (Anonymous 1980-84).

Commodity	Year	Insecti-cides	Fungi-cides	Herbi-cides	Other Pesticides	Total
Cherries	1980	10	6	4	2	22
(sweet)	1984	10	7	4	2	23
	Monitored	8	3	0	0	11
Peaches	1980	14	9	5	2	30
	1984	14	9	5	2	30
	Monitored	10	5	0	0	15
Strawberries	1980	12	6	6	3	27
	1984	12	5	6	4	27
	Monitored	10	1	1	0	12

Samples had already been prepared for market by the vendors at the time of collection and only edible tissues were analyzed.

Fruits were macerated and composited in a food chopper and subsamples were removed for analysis according to the following procedures.

(a) Organochlorine, organophosphorus, and synthetic pyrethroid insecticides, phthalimide fungicides, and dichloran. Fifty grams of macerated sample was blended with 250 mL of 2:1 acetonitrile-water and then filtered. A one-half aliquot was removed (PAM 1986), diluted with 500 mL water and 25 mL saturated NaCl solution, and partitioned with 2 X 50 mL dichloromethane. The dichloromethane was dried by percolation through anhydrous Na_2SO_4, iso-octane was added and concentrated just to dryness using a rotary vacuum evaporator. The residue was redissolved in 5.0 mL iso-octane.

A portion of the concentrated sample (4.5 mL) was cleaned up and fractionated for organochlorine and pyrethroid insecticides and phthalimide fungicides according to the procedure of Braun and Stanek (1982) and Mills *et al.* (1972). The remaining portion was used without clean-up for determination of organophosphorus insecticides.

Determinations were made by gas-liquid chromatography; detection limits are shown in Table 2. Average recoveries ranged from 85 to 97%.

(b) Methamidophos and oxydemeton-methyl. Methamidophos was extracted according to the procedure described by Braun *et al.* (1980). Oxydemeton-methyl was extracted as in (a) above along with the other organophosphorus insecticides. A portion of the extract was oxidized to convert oxydemeton-methyl to its sulfone prior to analysis (Thornton *et al.* 1977).

Table 2. Pesticide groups and individual pesticides used between 1980 and 1984 and included in monitoring of fruit for that period.

Pesticide Group	Insecticides	Detection Limit (mg/kg)
Organochlorine[1] insecticides (OCI)	(dieldrin), lindane	0.001
	(DDT,DDE,TDE) endosulfan[2],	
	chlordane[3], dicofol,	0.002
	methoxychlor	0.01
Organophosphorus insecticides (OPI)	diazinon, mevinphos, demeton, dimethoate, ethion, malathion	0.005
	parathion	0.01
	phosalone	0.05
	naled	0.1
	phosmet	0.2
	azinphosmethyl	0.5
Special (OPI)	oxydemeton-methyl	0.1
	methamidophos	0.02
N-methylcarbamate insecticides (MCI)	carbaryl, carbofuran, pirimicarb	0.01
Chlorophenoxy acid herbicides (CPH)	chloramben, 2,4-D, 2,4-DB, dichlorprop, MCPA, MCPB	0.01
Chlorobenzoic acid herbicides (CBH)	dicamba, diclofop-methyl	0.01
Organochlorine fungicides (OCF)	captan, captafol, folpet, dichloran	0.002
Special (OCF)	chlorothalonil	0.01
Dithiocarbamate fungicides (DCF)	maneb, mancozeb, metiram, zineb, ziram, thiram	0.01

[1]dieldrin not used since 1969; DDT and TDE not used since 1970
[2]total endosulfan - endosulfan I, II, and sulfate
[3]total chlordane - cis- and trans-chlordane, heptachlor epoxide, and nonachlor

(c) N-methylcarbamate insecticides. Fifty grams of macerated vegetable tissue was extracted as described in (a) above. All compounds were determined by capillary column GC with a nitrogen-phosphorus detector as described by Ripley and Braun (1983). Recoveries ranged from 85-110%.

(d) Chlorothalonil. Chlorothalonil was determined using the procedure (c) or as described by Northover and Ripley (1980). The latter analysis included the parent compound and the 4-hydroxy metabolite with recoveries of 85-88%.

(e) Dithiocarbamate fungicides. These fungicides were determined as their zineb equivalent using the carbon disulfide evolution technique based on the method of Pease (1957) with the modifications described by Ripley (1979).

(f) Chlorophenoxy and chlorobenzoic acid herbicides. Fifty gram samples of vegetables were extracted and residues were quantified by gas chromatography using a procedure described by Yip (1971) and modified by Sirons et al. (1982). Mean recoveries for residues above 0.01 ug/g were 80%.

Duplicate field samples and internal laboratory checks were analyzed at random as an on-going quality assurance program. Confirmation techniques were applied when residues were high enough to allow alternative procedures to be used. These included (i) the use of element-specific GLC detectors, e.g. electrolytic conductivity (or Hall) detection in the Cl- or N-specific mode or flame photometric detection in the P- or S-specific mode, (ii) the use of alternate-column GLC, e.g. using column packings of different polarity so that characteristic retention times were significantly changed, or (iii) with a capillary gas chromatograph and mass selective detector using either full scan or single- or multiple-ion monitoring. Residue results are uncorrected for recoveries.

RESULTS AND DISCUSSION

Between 1980 and 1984, 179 fruit samples were analyzed for insecticides, fungicides and herbicides. Pesticide residues appear in Table 3 and are compared with the maximum residue limits (MRL) appearing in the Food and Drug Act and Regulations (Anonymous 1985). Residue data are split into the field years 1980-82 and 1983-84 since some MRLs were changed and different analyses were performed.

Residues of the insecticides carbaryl, dicofol, endosulfan, phosalone and phosmet, the fungicides captan and chlorothalonil, and the herbicide 2,4-D were found in many of the 36 samples of sweet cherries analyzed. No sweet cherries contained residues that exceeded the maximum residue limit and the detected residues represented only between 1% and 20% of the MRL. In 1983, the MRL of captan was reduced from 40 to 5 mg/kg by Canada Gazette (Part II, Volume 117, No. 7 page 1225, 13 April, 1983). Despite this change, residues of captan were well below the new level.

Table 3. Fruit monitoring for insecticide, fungicide and herbicide residues in Ontario, 1980-84.

Commodity Years	Composite Samples	Group[1]	Pesticides No Residues Detected	Identified	Above or Below MRL Number	(mg/kg)	Pesticide MRL (mg/kg)
Cherries Sweet 1980-82	26	OCI	5	Dicofol	13	0.07 ± 0.08	3.0
				Endosulfan	13	0.02 ± 0.14	2.0
				DDE	2	0.003 ± 0.001	0.1
		OPI	11	Phosalone	10	0.25 ± 0.36	6.0
				Phosmet	6	0.04 ± 0.05	7.0
		OCF	6	Captan	20	0.70 ± 1.24	40.0
		CPH, CBH	10	2,4-D	1	0.01	0.1
1983-84	10	OCI	4	Dicofol	4	0.10 ± 0.14	3.0
				Endosulfan	6	0.01 ± 0.01	2.0
		OPI	2	Phosalone	8	0.06 ± 0.05	6.0
		MCI	5	Carbaryl	1	0.33	10.0
		OCF	1	Captan	9	0.44 ± 0.33	5.0
		OCF Special	0	Chlorothalonil	5	0.02 ± 0.01	0.1
		DCF	5	None	0	- -	7.0
Peaches 1980-82	26	OCI	5	Dicofol	16	0.10 ± 0.18	3.0
				Dicofol	2	4.8 ± 2.1	3.0
				Endosulfan	14	0.12 ± 0.10	2.0
		OPI	8	Parathion	2	0.05 ± 0.05	1.0
				Phosmet	18	1.93 ± 1.28	10.0
		OPI Special	8	Azinphosmethyl	5	0.90 ± 0.34	2.0
				Azinphosmethyl	2	2.3 ± 0.1	2.0
		OCF	4	Captan	22	1.64 ± 2.04	40.0
		CPH, CBH	19	MCPA	1	0.01	0.1

1983-84	10	OCI	0	Dicofol	7	0.19 ± 0.22	3.0
				Endosulfan	9	0.03 ± 0.02	2.0
		OPI	4	Phosmet	6	0.58 ± 0.54	10.0
		MCI	1	Carbaryl	4	0.22 ± 0.30	10.0
		OCF	1	Captan	9	0.59 ± 0.74	5.0
		DCF	5	None	0	- -	7.0
		DCF Special	5	None	0	- -	0.1
Strawberries	60	OCI	20	Endosulfan	40	0.10 ± 0.09	1.0
1980-82		OPI	60	None	0	- -	-
		MCI	13	Carbofuran	3	0.01 ± 0.01	0.4
		OCF	2	Captan	58	2.81 ± 1.55	25.0
		CPH, CBH	6	2,4-D	3	0.02 ± 0.01	0.1
				MCPA	1	0.02	0.1
1983-84	47	OCI	22	Endosulfan	24	0.15 ± 0.13	1.0
				Methoxychlor	2	0.004 ± 0.001	14.0
		OPI	46	Dimethoate	1	0.04	1.0
		MCI	32	Carbofuran	9	0.09 ± 0.4	0.4
				Carbofuran	1	4.5	0.4
		OCF	9	Captan	37	1.22 ± 1.30	5.0
				Captan	1	7.1	5.0
Total	179	OCI, OPI, OCF (OPI - Special - 26, OCF - Special - 10)					
1980-84	69	MCI					
	41	CPH, CBH					
	5	DCF					

[1]OCI - organochlorine insecticides, OPI - organophosphorus insecticides, MCI - methylcarbamate insecticides OCF - organochlorine fungicides, DCF - dithiocarbamate fungicides, CPH - chlorophenoxy herbicides, CBH - chlorobenzoic herbicides.

In the 1980-82 period, two insecticides, dicofol and azinphosmethyl, were found in violation in each of two of 26 peach samples. No violations were observed with peaches in the 1983-84 period. Other pesticides detected in the 36 samples of peaches but not in violation of the MRL were the insecticides endosulfan, parathion, phosmet and carbaryl, the fungicide captan, and the herbicide MCPA. These detected pesticide residues ranged from 1% to 20% of the MRL. The MRL for captan on peaches was reduced from 40 to 5 mg/kg at the same time that it was reduced for sweet cherries; no peaches violated this 5 mg/kg MRL.

Between 1980 and 1984, 107 samples of strawberries were analyzed and in that period two samples were found in violation of MRL. One occurred in 1983 involving captan and this violation was found within two months of the reduction in the MRL from 25 to 5 mg/kg. The second involved carbofuran and it also occurred in 1983. Other pesticides detected were well below the MRL and included the insecticides endosulfan and dimethoate and the herbicides 2,4-D and MCPA.

Between 1982 and 1984, a survey of 38 strawberry farms was undertaken to determine which pesticides were being used. Of the five fungicides and the 12 insecticides recommended (Table 1) to growers, only four fungicides and five insecticides were actually used (Table 4). The major fungicides being applied for crop protection were captan and benomyl and the major insecticides were azinphosmethyl, carbofuran and endosulfan. All except benomyl were included in the analytical procedures used in this monitoring study.

Table 4. Survey of fungicides and insecticides used by 38 strawberry growers.

Pesticides Used	Growers Number	(%)	Residue (mg/kg) Mean ± SD	MRL[1] (mg/kg)
Fungicides				
Benomyl	21	55	NA[2]	5.0
Captan	32	84	0.87 ± 3.67	5.0
Anilazine	2	5	NA[2]	20.
Dodine	3	8	NA[2]	5.0
Insecticides				
Azinphosmethyl	14	37	<0.5	1.0
Carbofuran	19	50	0.28 ± 1.02	0.4
Dimethoate	1	3	0.036	1.0
Endosulfan	20	53	0.18 ± 0.14	1.0
Methoxychlor	2	5	0.004 ± 0.001	14.

[1]MRL - maximum residue limit
[2]NA - not analyzed

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