

FQPA-targeted Pesticide Residue Study

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Introduction

As a result of the passage of the 1996 Food Quality Protection Act (FQPA), a potential crisis faces agriculture as pesticide tolerances are reassessed using stricter guidelines. Reassessment of tolerances under these new guidelines partially depends on assessing aggregate exposure to pesticide residues from food, drinking water, and residential sources. Thus, the Environmental Protection Agency (EPA) is interested in information about pesticide residues. Although some information about pesticide residues in food sources is available from the Pesticide Data Program (PDP), information linking actual pesticide use at the grower level to pesticide residues is lacking. This study was intended to bring together federal and state regulatory agencies with research, extension, commodity, and grower groups to develop residue information to feed into the tolerance reassessment process. The goal was to collect and test samples from important minor use crops in Michigan, and in some cases to track residues through processing. When possible, the study related pesticide residue levels to actual pesticide applications indicated in spray records. Another goal was to show how mitigation strategies, including implementation of alternatives, influenced the potential for pesticide residues. This is of particular importance, given FQPA.

A total of 245 samples were collected from both grower farms and university research plots. The following commodities were sampled: apple, asparagus, blueberry, tart cherry, cucumber, grape, peach, and potato. Growers and researchers used a range of pesticide application regimes that included mitigation strategies for FQPA-targeted pesticides (organophosphates, carbamates, and B2 carcinogens). Pesticide spray records were obtained from growers or researchers, as appropriate. The identities of cooperating growers and processors were kept confidential by passing samples and spray records through intermediaries, such as consultants and extension agents, and by coding samples with numbers rather than names. The Michigan Department of Agriculture laboratory analyzed samples for at least 65 pesticide residues. In some cases, the laboratory tested for additional products used on specific commodities or in certain experimental plots. Results of this study are contained in eight individual reports, one for each commodity. Each report contains the following sections: an introductory description of the crop and its importance in Michigan; a description of several key pests; a description of several of the pesticides used by the growers in this study; materials and methods for the study; grower spray timelines if applicable; pesticides labeled for use on each crop in 1998; the residue results, in tables and in text; key references; and the list of pesticides included in the residue analysis. These individual reports are still evolving as we obtain additional spray records and examine data in different ways.

Below is a summary of the some of the highlights of each report.

Apples

- 32 samples: 14 research and 18 grower
- Samples analyzed for 67 pesticides; 3 were detected, all below current tolerances
- Azinphos-methyl (Guthion) was used but not detected
- Methyl parathion (Pennacp-M) was not used and not detected

Asparagus

- 57 samples: 40 research and 17 grower
- Samples analyzed for 67 pesticides; 2 were detected, all below current tolerances
- The Section 18 product chlorothalonil (Bravo) applied to ferns in 1997 was not detected on spears in 1998
- Carbaryl (Sevin), used for asparagus beetle control, was detected on 49% of fresh, unwashed samples
- No pesticides were detected in processed (canned) samples

Blueberries

- 4 samples: 1 research and 3 grower (“U-pick”)
- Samples analyzed for 66 pesticides; 3 were detected, all below current tolerances
- Azinphos-methyl (Guthion) was not detected when used

Cucumber

- 3 samples: all grower
- Samples analyzed for 68 pesticides; none were detected
- Insect and disease pressure in 1998 was low, thus little pesticide was applied to the crop

Grapes

- 20 samples: all grower
- Samples analyzed for 66 pesticides; 5 were detected, all below current tolerances
- Although EBDC fungicides were used by all growers, no residue was detected
- Most growers used methyl parathion (PennCap-M), but residue was detected in only 1 sample
- Most growers used carbaryl (Sevin), and residue was detected in 45% of samples

Peaches

- 58 samples: all grower
- Samples analyzed for 68 pesticides; 9 were detected, all below current tolerances
- Grower samples were off-tree, washed, brushed, peeled, and processed (canned)
- In general, washing and brushing reduced residue levels
- No residues were found in peeled or processed product

Potato

- 38 samples: all research, representing 19 different fungicide application regimes
- Samples analyzed for 72 pesticides; none were detected
- Despite a wide range in fungicide types and spray regimes, no residues of chlorothalonil (Bravo), EBDCs, metalaxyl (Ridomil), or propamocarb hydrochloride (Tattoo) were found

Tart Cherries

- 33 samples: 12 research and 21 grower
- Samples analyzed for 65 pesticides; 7 were detected, all below current tolerances
- Grower samples were off-tree, washed, and processed (canned), but there was no pattern to the residue detections.

Apples

Introduction

Apple trees belong to the family Rosaceae, with domestic varieties of the species *Malus domestica*. Like pears, apples are called “pomes,” because of the papery membrane surrounding the core. Today, most apple varieties (e.g., ‘Red Delicious’, ‘Gala’, ‘Jonathon’, etc.) are grafted to dwarfing and semi-dwarfing rootstocks. These smaller stature trees tend to require less pesticides but produce more fruit per acre than the larger trees planted by earlier generations of apple growers. Depending on variety, rootstock and other production factors the trees do not bear their first crop until 2 to 7 years after planting. The trees are then kept in production for many years and may be capable of producing fruit for several decades. Trees bloom in the spring, with harvest in late summer through fall. Apples have the longest harvest season of any Michigan fruit, starting about mid-August for the late-summer varieties and extending into late October and early November in some years for the latest fall varieties.

Michigan apples were grown on 55,000 acres in 1997, which is unchanged for the last five years. Production was up from 1996, with 1.05 billion pounds harvested in 1997. This quantity exceeds all other Michigan fruits combined, with Red Delicious as the primary variety grown (1.9 million trees). Michigan ranks third in the nation for apple production. Most apples (71%) are processed, either canned (27%), frozen (14%), or made into juice and cider (30%). The total farm-gate value of apple production was \$99.8 million in 1997.

Major Pests

Codling Moth (*Cydia pomonella*). This moth can be a very serious insect pest of apples. Larvae overwinter under tree bark, with the first moths appearing when the petals fall from the apple blossoms. Eggs are then laid on the developing fruit. Larvae cause damage either by deep entries into the blossom end of the fruit with tunneling inside the fruit, or by aborted tunneling in the sides of the fruit, with the second generation of larvae causing the most damage.

Apple Maggot (*Rhagoletis pomonella*). This fly is another serious insect pest of apples. Pupae overwinter in the soil, with flies emerging from late June to early September. Eggs are laid by the female in the sides of the apple; these puncture wounds cause dimples in the fruit surface. Hatching maggots tunnel extensively through the fruit, leaving brown trails. These trails can cause interior tissue to disintegrate, or cause the fruit to drop prematurely. The primary means of control is to kill the flies as they enter orchards to mate and lay eggs.

Plum Curculio (*Conotrachelus nenuphar*). This weevil is a destructive pest of many tree fruits. Adult beetles overwinter in debris outside of the orchard, moving among the trees in the spring bloom period. Injury by this insect can be by: (1) wounds from feeding and egg laying in the spring, causing crescent-shaped scars or bumps on fruit; (2) internal damage from larval feeding and tunneling; (3) premature fruit drop; and (4) beetle feeding scars in mature fruit.

Oriental Fruit Moth (*Grapholita molesta*). This insect is becoming a significant pest of apples, although their primary hosts are stone fruits. The larvae are often confused with those of codling moth, and thus may be a more serious pest of apples than was previously thought. First-generation adults appear in early May, with their larvae feeding on actively growing terminals and fruit. Second-generation adults appear in mid-July; their larvae feed internally on the fruit. Third-generation adults appear in late August, and their larvae also feed in the fruit.

Oblique-Banded Leafroller (*Choristoneura rosaceana*). Overwintering larvae feed on the developing blooms, fruit, and foliage. Moths emerge during June, and then lay eggs on the

leaves. The second generation feeds on foliage and fruit. This pest has developed significant resistance to organophosphate insecticides in some parts of Michigan. The fall overwintering generation of larvae can also feed on fruit in September.

European Red Mite (*Panonychus ulmi*). This mite is a significant pest of deciduous fruit trees around the world. Damage is due to the mites feeding on the foliage, causing leaf bronzing. On heavily infested trees, this bronzing causes trees to produce fewer and weaker overwintering buds, affecting tree vigor the next year.

White Apple Leafhopper (*Typhlocyba pomaria*). Like the mites, damage by this sucking insect is from removal of chlorophyll from leaf cells, which indirectly affects both the quality of the fruit and the formation of buds for the next spring. Second-generation leafhoppers directly damage the fruit from the accumulation of leafhopper excrement, which is difficult to remove in dry seasons.

Apple Scab (*Venturia inaequalis*). This fungus is one of the most common and serious diseases of apple and flowering crabapple. The disease causes premature defoliation and a reduction in the number and quality of flowers the year following defoliation, and can predispose trees to winter injury and other diseases. Fungal spores may also attack the fruit at any stage of development. Infection early in the spring results in blighted blossoms and fruit drop. Symptoms normally develop 9 to 17 days after infection; at this time the fungus can infect leaves or fruit throughout the summer during favorable (wet, warm) weather.

Fire Blight (*Erwinia amylovora*). This bacterium, while occurring sporadically, can cause significant epidemics in some years, killing fruit-bearing spurs and sometimes entire trees. Infected flowers and leaves turn brown to black, with the stem ultimately dying. Infected fruit turn black and shrivel, oozing bacterial liquid. Cankers develop in the larger limbs and trunk, which allow the bacteria to survive the winter. If conditions are favorable the next year, the entire limb or the tree may die. Hard rains (especially storms containing hail) and flower-visiting insects (e.g., pollinators) help spread this disease.

Powdery Mildew (*Podosphaera leucotricha*). This fungus can cause significant damage to apple orchards. Fungal infection can cause death of leaf shoots, flowers (with decrease in yield), and overwintering buds, as well as damage the fruit directly (russetting). Fungal spores do not require leaf wetness to germinate, only high humidity with higher temperatures. Fungicides must be applied preventatively to control this disease.

Pesticides Used

1. Azinphos-methyl (Guthion)

Non-systemic, broad-spectrum organophosphate insecticide used to control oblique-banded leafroller, apple maggot, oriental fruit moth, and codling moth.

Oral LD₅₀ (rats) = 5 mg per kg body weight

Dermal LD₅₀ (rabbits) = 220 mg per kg body weight

Persistence in soil dependent upon soil type, ranging from 30-d to 1-yr breakdown time. On vegetation, the approximate residual period is 1-3 wks.

7 day PHI.

2. Carbaryl (Sevin)

Broad-spectrum, systemic, cholinesterase inhibitor, widest use of any insecticide; used to control white apple leafhopper.

Oral LD₅₀ (rats) = 307 mg per kg body weight

Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Insecticidal properties on crop for 3-10 days. Half life in aerobic soil 7 d, anaerobic 28 d.
3 day PHI

3. Chlorpyrifos (Lorsban)

This is a heterocyclic organophosphate contact poison used to control oriental fruit moth, codling moth, apple maggot, and plum curculio.

Oral LD₅₀ (rats) = 135 mg per kg body weight

Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Moderately persistent but relatively immobile. The half-life ranges from 11-141 days depending on soil type, soil pH, and aerobic conditions.

28 day PHI

4. Dimethoate (Dimethoate)

Systemic organophosphate, used to control aphids, leafhoppers, mites, apple maggot, and codling moth.

Oral LD₅₀ (rats) = 250 mg per kg body weight

Dermal LD₅₀ (rabbits) = 150 mg per kg body weight

Rapidly biodegradation, with a half-life in soil of 2.5-16 days

28 day PHI

5. Endosulfan (Thiodan)

Cyclodiene organochlorine, used to control aphids and scale insects.

Oral LD₅₀ (rats) = 18 mg per kg body weight

Dermal LD₅₀ (rabbits) = 74 mg per kg body weight

Endosulfan breaks down within 4 weeks, but the breakdown isomers may be persistent in the soil and on vegetation

21 day PHI

6. Imidacloprid (Provado)

A systemic, chloro-nicotinyl insecticide for the control of sucking insects, such as leafhoppers and leafminers.

Oral LD₅₀ (rats) = 450 mg per kg body weight

No dermal irritation

Half-life of imidacloprid in soil is 48-190 days, depending on the amount of ground cover

7 day PHI

7. Methomyl (Lannate)

A systemic carbamate insecticide used to control codling moth, apple maggot, leafminers, and oblique-banded leafroller (resistant to organophosphates).

Oral LD₅₀ (rats) = 17 mg per kg body weight

Dermal LD₅₀ (rabbits) = 1000 mg per kg body weight

The dissipation half-life is 3-6 wks. in soil. It is highly soluble in water, increasing the chances for ground water contamination.

14 day PHI

8. Phosmet (Imidan)

Non-systemic, organophosphate insecticide. Used to control plum curculio and oriental fruit moth.

Oral LD₅₀ (rats) = 147 mg per kg body weight

Dermal LD₅₀ (rabbits) = 3160 mg per kg body weight

Half-life in sandy loam soil 3-19 d, with increasing rates of breakdown in higher pH.

7 day PHI

9. Pyridaben (Pyramite)

Contact toxin, used to control mites and leafhoppers.

Oral LD₅₀ (rats) > 2000 mg per kg body weight

No dermal toxicity

Persists on foliage 40-55 days.

25 day PHI

10. Benomyl (Benlate)

A systemic fungicide with a wide spectrum of activity; in apples, used for scab (not effective in Michigan due to resistance), powdery mildew, and summer diseases (sooty blotch and fly speck).

Oral LD₅₀ (rats) > 10,000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight

Benomyl is strongly bound to soil. The half-life is 6-12 months.

14 day PHI

11. Captan

Non-systemic sulfenimide fungicide, used to control apple scab and summer diseases.

Oral LD₅₀ (rats) = 9000 mg per kg body weight

No dermal irritation

Half-life in soil 1-10 d, with activity on foliage for 23d

0 day PHI

12. Copper (Kocide, Champ, COCS)

Used as copper sulfate with lime and as copper hydroxide; protectant fungicide against scab and fire blight.

Oral LD₅₀ (rats) = 300 (sulfate) or 1000 (hydroxide) mg per kg body weight

Dermal irritant

No PHI restrictions if applied per label instructions.

13. EBDC (Polyram, Dithane, Manex, Penncozeb)

Nonsystemic fungicide, used to control apple scab and summer diseases (no use after petal fall).

Oral LD₅₀ (rats) > 8000 mg per kg body weight

No dermal toxicity

Half-life is assumed to be 4-8 weeks under normal field conditions.

77 day PHI

14. Fenarimol (Rubigan)

Pyrimidine systemic fungicide, can be used both preventatively and as a curative, to control apple scab and powdery mildew.

Oral LD₅₀ (rats) > 2500 mg per kg body weight

Dermal LD₅₀ (rabbits) > 2000mg per kg body weight

30 day PHI

15. Myclobutanil (Nova)

A systemic fungicide with curative and protective qualities, used to control scab and powdery mildew.

Oral LD₅₀ (rats) = 1600 mg per kg body weight

Dermal LD₅₀ (rabbits) > 5000 mg per kg body weight

14 day PHI.

16. Streptomycin (Agrimycin)

Antibiotic, used to control fire blight, often applied with fungicides in preventative program.

Oral LD₅₀ (rats) > 9000 mg per kg body weight

No dermal toxicity

50 day PHI

17. Triadimefon (Bayleton)

Systemic fungicide with protective and curative properties, for control of powdery mildew.

Oral LD₅₀ (rats) = 363 mg per kg body weight

Dermal LD₅₀ (rabbits) > 1000 mg per kg body weight

The half-life in soil is 6-18 d.

45 day PHI.

18. Ziram

Non-systemic dithiocarbamate fungicide used to control apple scab and summer diseases.

Oral LD₅₀ (rats) = 1400 mg per kg body weight

Dermal LD₅₀ (rabbits) > 6000 mg per kg body weight

In the air and soil Ziram is readily degraded by ultraviolet light. Biodegradation may be slow due to the toxicity to bacteria.

14 day PHI

Materials and Methods—see Appendix A

Grower and Experimental spray application timelines—see Figure 1

Results and Discussion

A total of 32 apple samples were examined for residues, 18 from commercial orchards and 14 from research plots at Michigan State University. All samples were tested for a total of 67 pesticides and metabolites (Appendix B). Three different pesticides were detected, all from commercial orchard samples. There were no residues detected for the additional pesticides listed in Appendix B.

Several fungicides and insecticides were labeled for use in 1998 (Table 1), and growers only used a little more than half of those available. While it appears that apple growers applied pesticides frequently (Fig. 1), they were often spraying every other row, which both decreased the total amount of product applied and provided continuous overlapping coverage for protection from pests.

Frequent applications of fungicides are required for effective control of fungal pathogens (Fig. 1). EBDC products were used in 11 of 12 grower orchards. The pre-harvest interval for these products is 77 days, yet growers typically apply them no closer than 116 days before harvest (Table 2). Despite the use by most growers, no EBDC fungicide residues were detected on the fruit (Table 2). Captan was used in 8 of the 12 commercial orchards (Table 2). Despite a zero-day pre-harvest interval, growers did not apply captan more than 36 days before harvest (Table 2). Captan was detected in only two samples (at 125 times below the current tolerance) (Table 2). Both of these samples were fresh product, and the corresponding processed sample from Grower #8 did not have a detectable residue of captan. No other fungicide residues were detected on any sample (Table 2).

Several organophosphates are registered for use against the destructive insect pests of apples (Table 1). In 1998, the organophosphates most commonly used by the growers in this study

were azinphos-methyl (11 orchards), chlorpyrifos (10 orchards), and phosmet (9 orchards). In all cases, the growers used significantly lower product amounts than the label allowed, and they also observed long pre-harvest intervals (Table 2, Fig. 1). The Michigan growers in this study did not use methyl parathion, another organophosphate often used in apple production. Phosmet was the only organophosphate residue detected (Table 2). Six grower samples were found to have detectable levels of phosmet, although the amounts detected were at least 14-times less than the current tolerance (Table 2). Two of these detections came from growers who had also submitted samples of processed apples, and in both cases, where there was residue on the fresh sample there was no residue on the processed sample.

Some alternatives to organophosphate insecticides were evaluated by both growers and researchers in 1998, and residue samples subsequently analyzed. Pheromone disruption of the codling moth was used to decrease the number of organophosphate sprays needed. For example, Grower #4 (Fig. 1) was able to eliminate two applications of azinphos-methyl and two applications of phosmet by using pheromone disruption for codling moth. Pheromone disruption was also used against the greater dogwood borer in MSU research plots (Fig. 1). Grower #3 (as a part of an on-farm research trial with MSU) used spinosad instead of late-season chlorpyrifos and azinphos-methyl (Fig. 1). Spinosad is a metabolite from fermentation of the bacterium *Saccharopolyspora spinosa*, and is being promoted as an insecticide that is less toxic on beneficial arthropods.

Two carbamate insecticides, carbaryl and methomyl, were used in 1998 (Fig. 1), although less frequently than the organophosphates. Three growers used carbaryl (Fig. 1), making one, two, or four applications. With pre-harvest intervals of 131+ days, carbaryl was not detected on apples from their orchards. Carbaryl residue was detected on one fresh and one processed sample, both from the same grower who did not record use of carbaryl. This detection might be due to a number of factors, such as residual pesticide in a spray tank or spray drift, or to contamination at some stage of sampling. We are continuing to investigate the possible sources of this pesticide. Methomyl was used by one grower with no residue detected (Table 2). The pyrethroid esfenvalerate was used on six orchards (Fig. 1) without detectable residue on any sample.

The research studies conducted by MSU used different pest management strategies, such as pheromone only or pheromone with two sprays of imidacloprid, two apple varieties with and without miticides, and one apple variety with or without captan (Fig. 1). Research samples were also analyzed for 67 pesticides and metabolites, although we did not test for the imidacloprid, spinosad, Comply, or Pyramite. There were no residues of any product detected in any sample from the experimental orchards.

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Table 1. Summary of Insecticides and Fungicides Registered for Use on Apples

Common Name	Trade name	Type ¹	Common Name	Trade name	Type ¹
<i>Used during 1998²</i>			<i>Not used in 1998²</i>		
azinthos-methyl	Guthion	OP	dithiocarbamate	Ferbam	B2
benomyl	Benlate	O	clofentezine	Apollo	O
captan	Captan	O	diazinon	Spectracide	OP
carbaryl	Sevin	Carb	dicofol	Kelthane	OC
chlorpyrifos	Lorsban	OP	dodine	Syllit	O
copper sulfate, copper hydroxide	Bordeaux mixture, Kocide	O	fenbuconazole	Indar	O
dimethoate	Cygon	OP	fenbutatin-oxide	Vendex	O
<i>Bacillus thuringiensis</i>	DiPel	O	formetanate hydrochloride	Carzol	O
EBDC	Penncozeb, Polyram, Dithane	B2	methyl Parathion	Penncap	OP
endosulfan	Thiodan	OC	oxamyl	Vydate	Carb
esfenvalerate	Asana	O	oxythioquinox	Morestan	O
fenarimol	Rubigan	O	permethrin	Pounce/Ambush	O
imidacloprid	Provado	O	propiconazole	Orbit	O
methomyl	Lannate	Carb	tebuconazole	Elite	O
myclobutanil	Nova	O	thiophanate-methyl	Topsin	O
phosmet	Imidan	OP	triflumizole	Procure	O
pyridaben	Pyramite	O			
streptomycin	Agrimycin	O			
triadimefon	Bayleton	O			
ziram	Ziram	O			

¹B2 = B2 carcinogen; Carb = carbamate; OP = organophosphate; OC = Organochlorine; O = other category.

²Refers to pesticides used by Michigan growers in this study.

Table 2. Potential and actual product use in apples, 1998, with pre-harvest intervals and residue found.

Product	<i>n</i> ^a	Maximum Rate ^b	Actual Total Use (rate X #app)		PHI ^c (days)	Actual PHI (days)		Tolerance (ppm)	Residue Results		
			Mean	Range		Mean	Range		No. (%) Positive Samples	Mean (ppm)	Range (ppm)
10 Growers: 4 + 2 IPM plots 6 (fresh + processed samples)	(12)										
azinphos-methyl	11	12 lb	5 lb	2-8.5	7	80	38-126	2	0	--	--
carbaryl	3	15 qt	2 qt	0.18-4	3	139	131-144	25	2 (11)	BQL ^d	BQL
chlorpyrifos	10	24 lb	3.4 lb	2-9	28	139	79-172	1.5	0	--	--
dimethoate	1	-- ^e	2 qt	--	28	98	--	2	0	--	--
endosulfan	2	3 lb	3 lb	2-4	21	107	99-115	2	0	--	--
methomyl	1	4.5 lb	1 lb	--	14	156	--	1	0	--	--
phosmet	9	30 lb	5.1 lb	2-13	7	44	26-70	10	6 (33)	0.22	0.1-0.7
captan	8	64 lb	15.6 lb	5-37	1	79	36-135	25	2 (11)	0.2	0.2
EBDC	11	24 lb	15.2 lb	3-32	77	138	116-165	variable	0	--	--
7 Experimental	(14)										
azinphos-methyl	5	12 lb	2.8 lb	2-3	7	83	82-85	2	0	--	--
carbaryl	1	15 qt	1 qt	--	3	115	--	25	0	--	--
chlorpyrifos	5	24 lb	3 lb	2-4.8	28	102	100-104	1.5	0	--	--
phosmet	5	30 lb	3 lb	3	7	69	68-70	10	0	--	--
captan	4	64 lb	9.8 lb	7.3-12.3	1	84	83-85	25	0	--	--
EBDC	4	24 lb	25 lb	18-30	77	98	68-131	variable	0	--	--

^aNumber of growers who recorded application of product during 1998, or number of experimental plots to which product was applied; Growers #3 and #4 each had a standard and an alternative orchard, for a total of 12 orchards.

^bBased on 1998 product label.

^cLabeled pre-harvest interval, in days.

^dBQL, below quantifiable limit.

^eNo maximum use restriction on 1998 label.

Figure 1. Grower and experimental spray records for apples, 1998

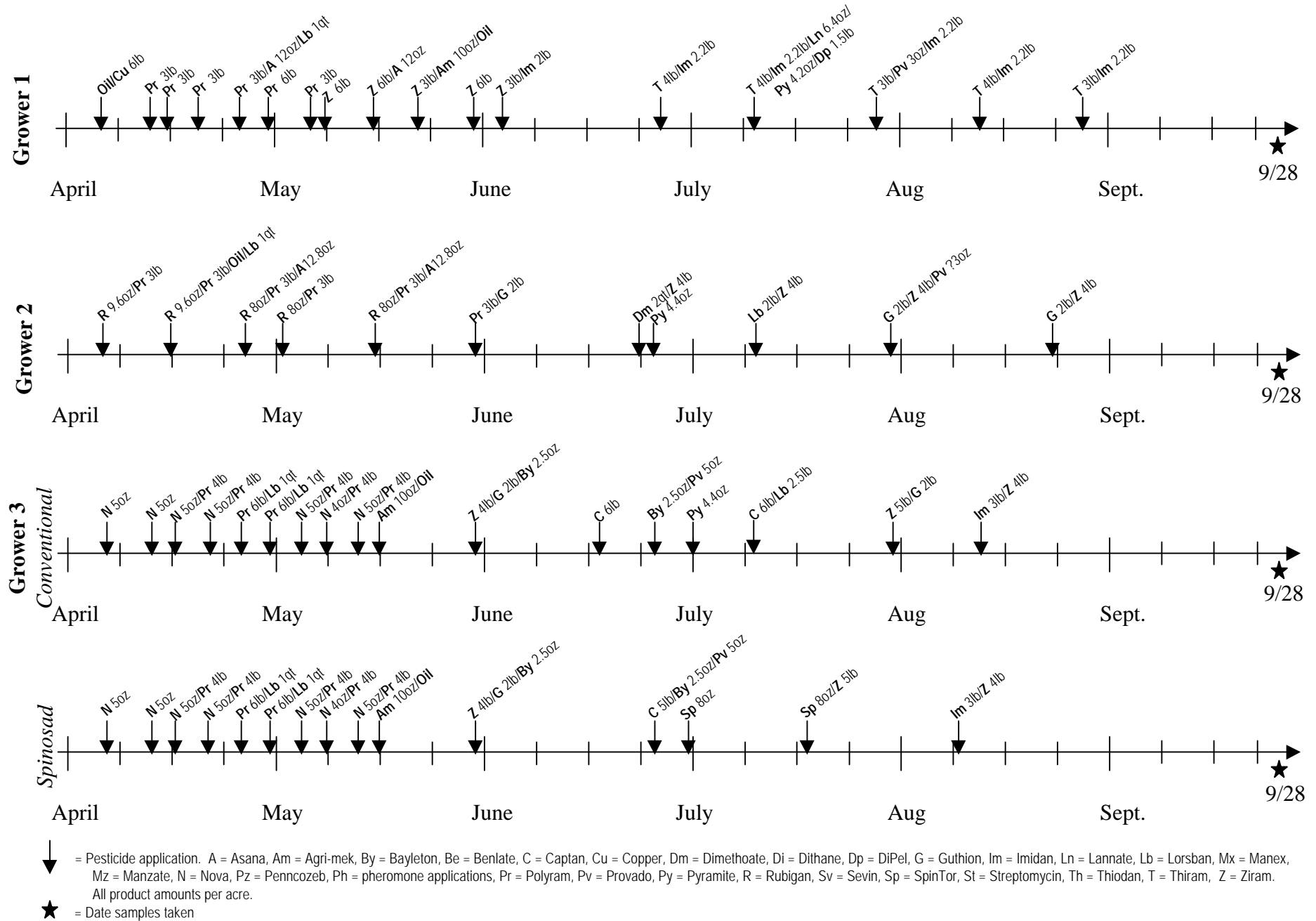


Figure 1, cont'd

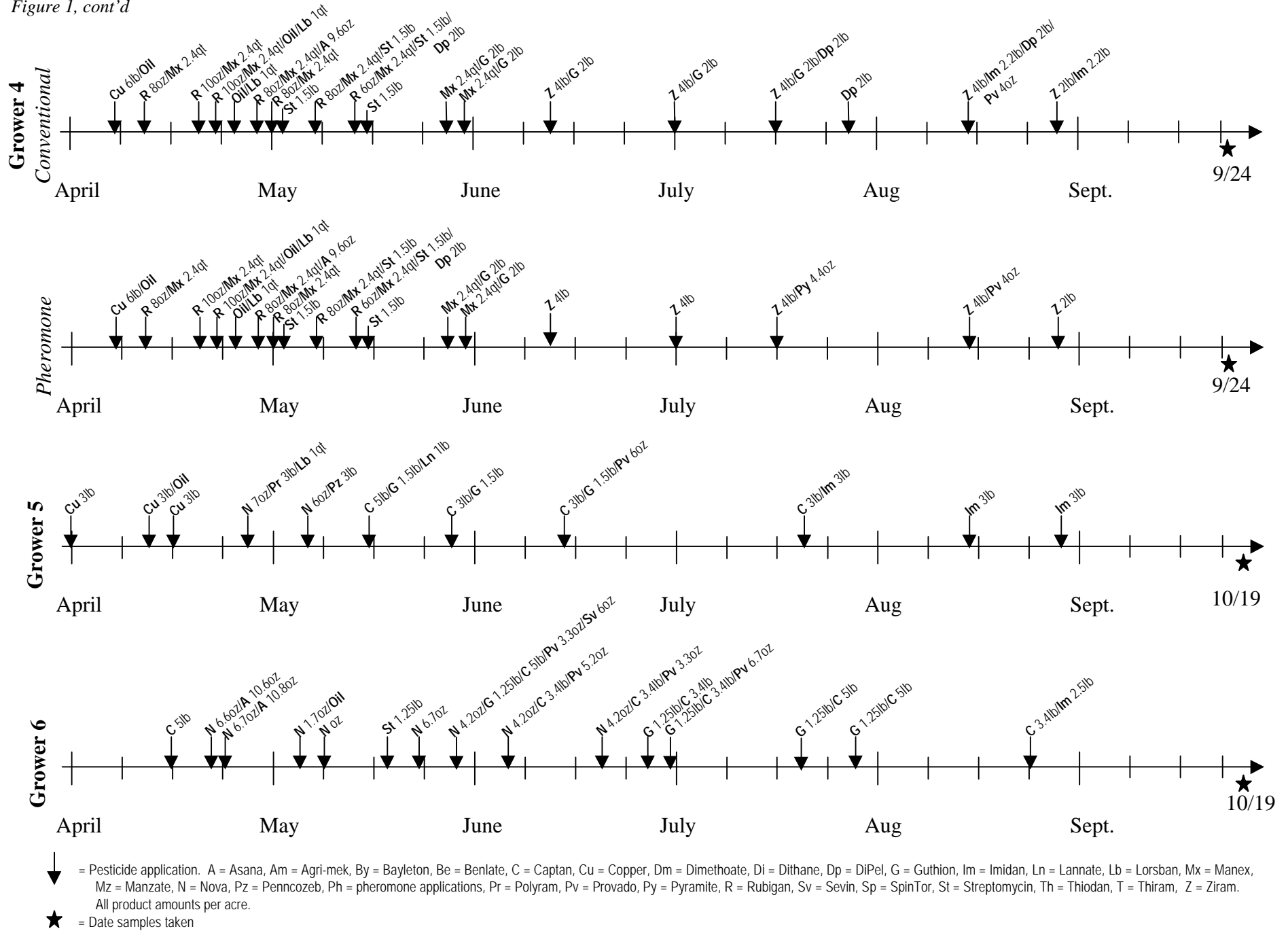


Figure 1, cont'd

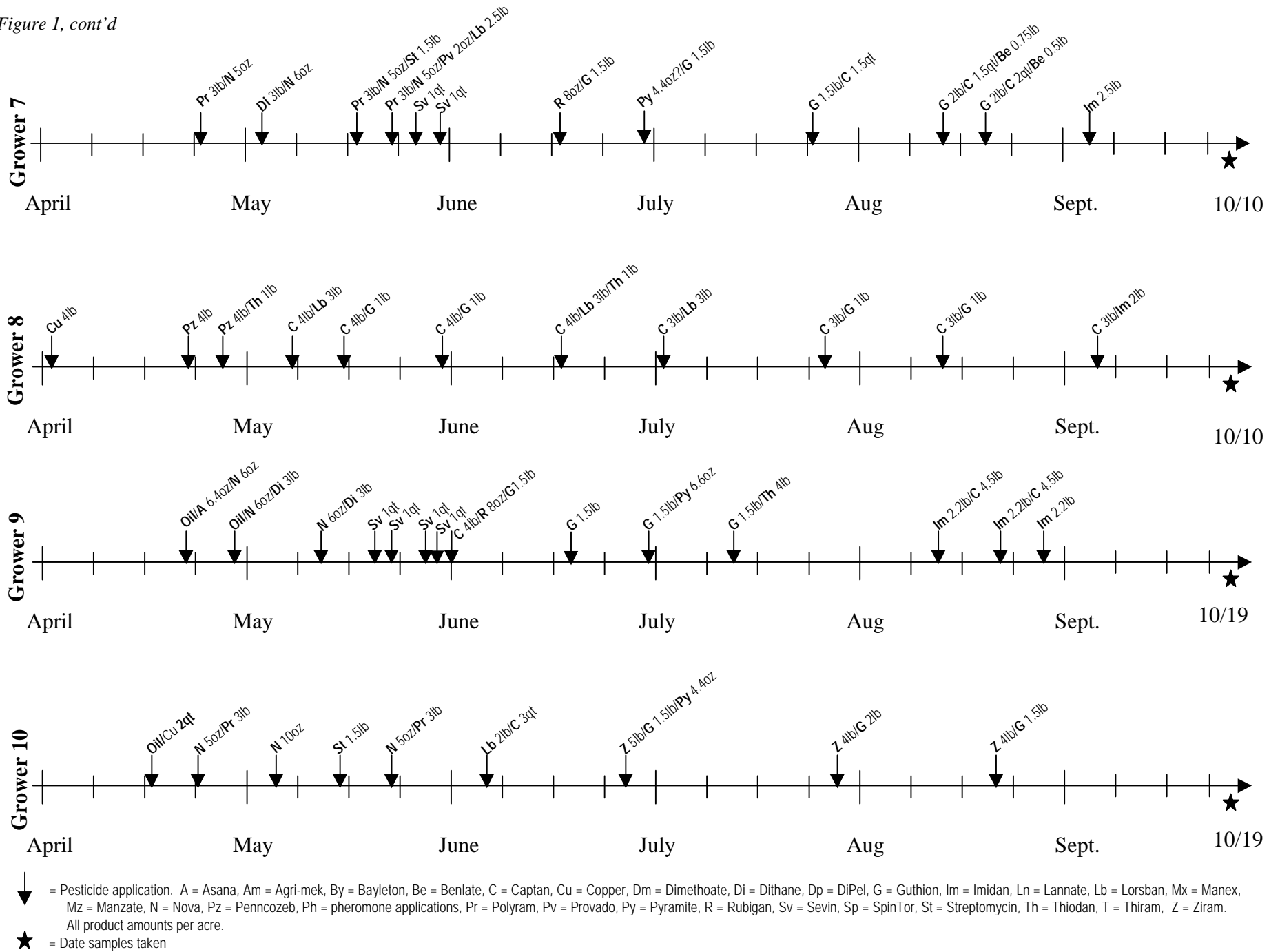


Figure 1, cont'd
Experimental

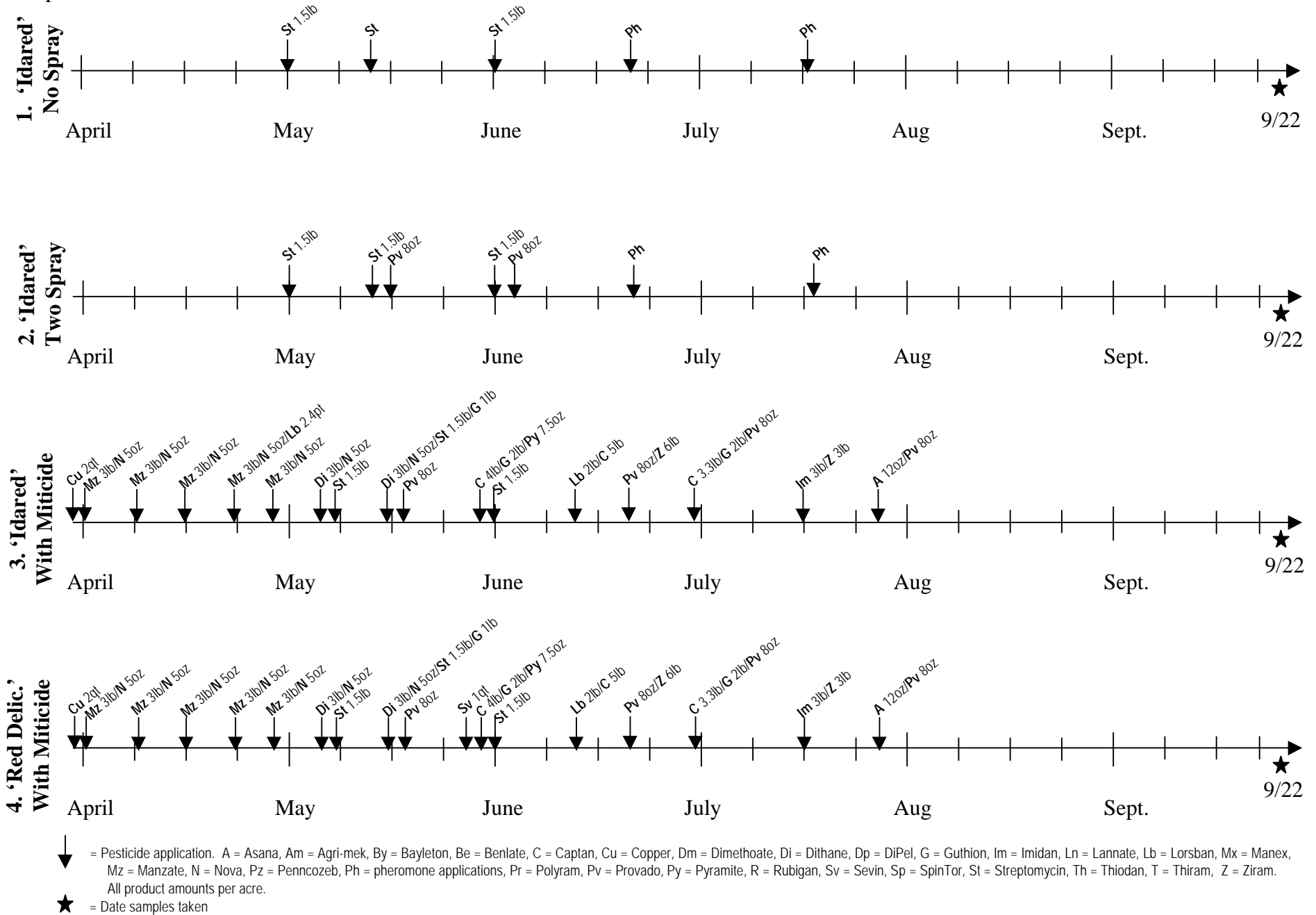
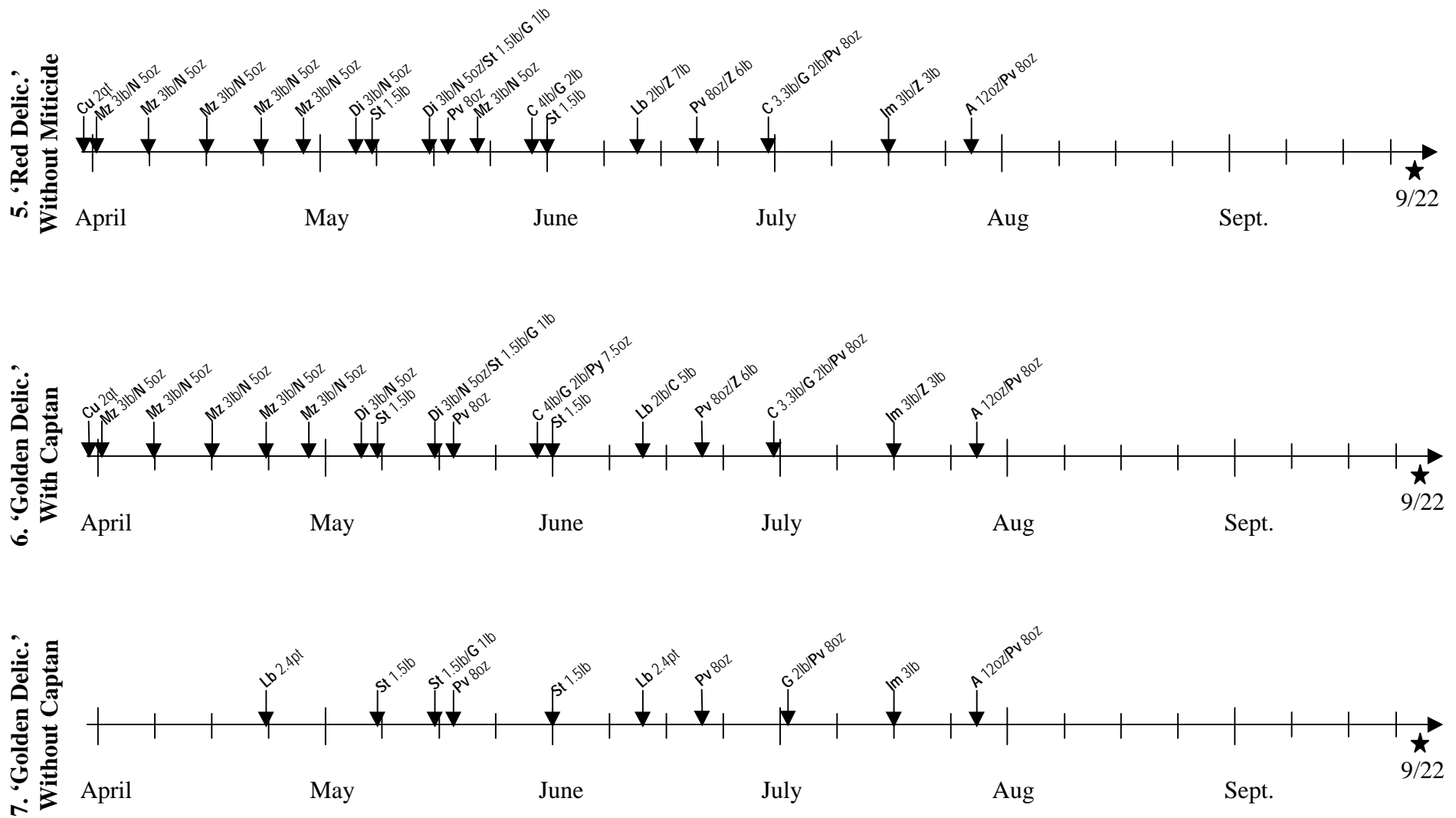


Figure 1, cont'd



↓ = Pesticide application. A = Asana, Am = Agri-mek, By = Bayleton, Be = Benlate, C = Captan, Cu = Copper, Dm = Dimethoate, Di = Dithane, Dp = DiPel, G = Guthion, Im = Imidan, Ln = Lannate, Lb = Lorsban, Mx = Manex, Mz = Manzate, N = Nova, Pz = Penncozeb, Ph = pheromone applications, Pr = Polyram, Pv = Provado, Py = Pyramite, R = Rubigan, Sv = Sevin, Sp = SpinTor, St = Streptomycin, Th = Thiodan, T = Thiram, Z = Ziram.

★ = Date samples taken

Appendix A – Materials and Methods

Harvest and handling

A. Research samples – pesticide trials:

The research plots of apples were located at the Clarksville Horticultural Extension Station (CHES) in Ionia County, Michigan. During the 1998 growing season, numerous pesticide trials were performed by the CHES staff. The following varieties and treatments were selected: 4 samples of ‘Idared’ with two applications of Provado and Comply; 4 samples of Idared without Provado or Comply applications; 1 sample of Idared and 1 sample of ‘Red Delicious’ with a Pyramite application on each; 1 sample of Idared and 1 sample of Red Delicious without Pyramite; 1 sample of ‘Golden Delicious’ with 3 applications of captan; and 1 sample of Golden Delicious without captan, for a total of 14 samples. Each sample consisted of approximately 15 apples. Pesticides used and the timing of the applications are shown in Figure 1.

These samples were taken immediately after harvest, between 22-24 September 1998, and were stored in plastic bags in a cooler (approximately 40°F) until 29 September. On that date, they were moved to the freezer (10°F) and stored there until residue analysis in October 1998.

B. Research samples – mating disruption:

One mating disruption (codling moth) trial and one spinosad trial were established with four Michigan apple growers (var. Red Delicious). Pesticides used and timing of the applications are shown in Figure 1. The six samples (approximately 15 apples per sample) were collected on 24 and 28 September 1998. One sample was taken from Growers #1 and #2, limited to conventional insecticide plots. One sample was taken from Grower #3 (spinosad trial) and from Grower #4 (mating disruption trial), and one from each of their conventional plots. The samples were randomly collected from the trees, and were immediately stored in plastic bags in the freezer (10°F) until residue analysis in October 1998.

C. Grower samples – raw vs. processed:

Six Michigan apple growers (#5-#10) participated in this study. Pesticides used and the timing of the applications are described in Figure 1. The apple varieties included Idared, Golden Delicious, ‘Jonathon’, and ‘Northern Spy’. Two 5-lb. samples were taken per grower on 19 November 1998: one sample of fresh apples from the cold storage of the processor, and one corresponding sample of peeled, sliced apples at the end of the processing line, just before freezing. The samples were immediately placed in plastic bags and stored in the freezer (10°F) until residue analysis in late November 1998.

Pesticide Residue Analysis

Laboratory Division of the Michigan Department of Agriculture performed the residue analysis. All samples were delivered to the laboratory in October and November 1998.

- I. The samples arrived in the laboratory frozen. They were stored in a freezer, then thawed prior to grinding and extraction.
- II. Preparation of the sample followed Section 102 of the Pesticide Analytical Manual (1997, Vol. 1, 3rd edition, U.S. Dept. of Health and Human Services, Public Health Service, Food and Drug Administration, pp.102-1—102-3). None of the samples were washed prior to analysis. For apples, the whole commodity was used after discarding stems.
- III. The extraction method used for most of the compounds was the “Luke II modified Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods.” This is a modification of the “Acetone Extraction Screening Method for Pesticide Residues in Non-Fatty, High Moisture Foods,” (Pesticide Analytical Manual, 1997, Vol. I, Sect. 302, U.S. Dept. of Health and Human Services, Food and Drug Administration). This is a multi-residue method for the analysis of organohalogen, organonitrogen, organophosphate, organosulfur, and carbamate pesticide residues in nonfatty, high moisture matrices, and returns both quantitative and qualitative results. Analysis of all the compounds except the carbamates was by Gas Chromatography/Mass Spectroscopy (GC/MS). Analysis of the carbamates was by Liquid Chromatography/Post-Column Derivatization/Fluorescence Detection, with carbaryl confirmation by MS.
- IV. The extraction and analysis method used for Benomyl was from “HPLC Fluorometric Analysis of Benomyl and Thiabendazole in Various Agricultural Commodities” (Bulletin #3650, E. J. Wojtowicz)
- V. Dithiocarbamates were analyzed using the Lowen and Pease method (G. Zweig [Ed.], 1964. Analytical methods for Pesticides, Plant Growth Regulators, and Food Additives, p. 65. *In* Fungicides, Nematocides and Soil Fumigants, Rodenticides, and Food and Feed Additives, Vol. III, Academic Press).
- VI. Limits of Detection were originally set by analyzing a set of spikes at or near the believed limit of detection. The standard deviation was determined and multiplied by the student’s T, at the 99% confidence level, to calculate the limit of detection. If the calculated limit of detection appeared excessively low or high, a set of spikes was

analyzed at a level thought to be more realistic, based on the signal to noise ratio. If all of these new spikes were detected and confirmed, then this became the new limit of detection. These were determined in one commodity and then assumed to be the same in other commodities unless spike recovery data indicated otherwise.

VII. Tolerances were from Duggan (1998, Pesticide Chemical News Guide, CRC Press LLC).

Appendix B—All pesticides included in the residue analysis of all apple samples.

Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)	Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)
3-Hydroxycarbofuran	M	0.002	none	Imazilil	F	2	none
Acephate	I	0.63	2 temporary	Iprodione	F	0.065	none
Alachlor	H	0.019	none	Lindane	I	0.063	1
Aldicarb	I	0.001	none	Linuron	H	0.078	none
Aldicarb Sulfone	M	0.002	none	Malathion	I	0.17	8
Aldicarb Sulfoxide	M	0.002	none	Methamidophos	I	0.30	none
Anilazine	F	0.15	none	Methidathion	I	0.055	none
Atrazine	H	0.025	none	Methomyl	I	0.002	1
Azinphos-Methyl	I	0.09	2.0	Methyl Parathion	I	0.058	1
Benomyl	F	0.06	7.0	Metolachlor	H	0.045	none
Captan	F	0.075	25	Mevinphos	I	0.15	0.5
Carbaryl	I	0.002	25 pending	Myclobutanil	F	0.14	0.5
Carbofuran	I	0.001	none	Omethoate	I	0.17	2
Chlorothalonil	F	0.005	none	Oxamyl	I	0.002	2
Chlorpropham	H	0.066	none	Oxyfluorfen	H	0.045	0.05
Chlorpyrifos	I	0.038	1.5	p,p'-DDE	M	0.013	0.1 revoked
Cypermethrin	I	0.20	none	p,p'-DDT	I	0.013	0.1 revoked
DCPA	H	0.013	none	p,p'-Dicofol	I	0.22	5
Diazinon	I	0.016	0.5	Pendimethalin	H	0.035	none
Dichloran	F	0.050	2.0 Section 18	Pentachloronitrobenzene	O	0.030	none
Dichlorvos	I	0.033	none	<i>cis</i> -Permethrin	I	0.028	none
Dieldrin	I	0.050	0.03	<i>trans</i> -Permethrin	I	0.038	none
Dimethoate	I	0.036	2	Phorate	I	0.042	none
Diphenylamine	F	0.014	10	Phosalone	I	0.045	10.0
Disulfoton	I	0.10	none	Phosmet	I	0.044	10
Endosulfan I	I	0.050	2.0	Phosphamidon	I	0.28	1
Endosulfan II	I	0.060	2.0	Propargite	I	0.050	3
Endosulfan Sulfate	M	0.075	2.0	Simazine	H	0.035	0.25
Ethion	I	0.011	2.0	Terbufos	I	0.025	none
Ethoprop	I	0.035	none	Thiabendazole	I	2	10
Ethyl Parathion	I	0.055	1	Triadimefon	I	0.17	1.0
Fenamiphos	I	0.2	0.25	Trifluralin	H	0.013	none
Fenvalerate	H	0.070	2.0	Vinclozolin	F	0.038	none
Hexazinone	H	0.15	none				

^aF = Fungicide, H = Herbicide, I = Insecticide, M = Metabolite (break-down product), O = Other, *e.g.*, contaminant of the production process.

Asparagus

Introduction

Asparagus (*Asparagus officinalis*) is a perennial plant in the Lily family. New plantings are made from root crowns, and take 3-4 years from establishment until harvesting can begin. Spears, the edible portion, emerge in the spring, with each crown producing multiple spears. Spears (9" height) are harvested every 1-3 days, from late April to mid-June in the north central growing region of the country. After harvest season, the crowns are left to produce additional spears that elongate into tall (> 4') fern-like plants. Over the remainder of the summer, the healthy green growth converts photosynthates into starches, which are stored in the roots. This starch storage provides the crown with energy the next spring to put up spears. Healthy asparagus plants can continue to produce spears of marketable quality for 10 years or more.

In 1998, Michigan growers harvested 17,500 acres of asparagus, which represents 23% of the total acreage grown to asparagus in the United States. Michigan ranks third in the nation for asparagus production, producing up to 25 million pounds annually. The 1998 yield was 1,600 lb per acre, up 3% from the previous year. The state annual average is 1,700 lb, but on new plantings the potential harvest can be as high as 3,000 lb per acre. Most (85%) of Michigan asparagus is targeted for processing, with 28% frozen and the remainder canned as cuts, tips, or spears. Total 1998 value for processed asparagus was \$14.8 million. While fresh market has a slightly higher value per pound, only 15% of Michigan asparagus was sold in this fashion. The total value of Michigan asparagus for 1998 was \$17.5 million.

Major Pests

Common Asparagus Beetle (*Crioceris asparagi*). Beetles overwinter as adults in field debris, emerging in the spring during spear harvest. After mating, females lay their eggs on the spears, resulting in loss of yield from discard of an unmarketable product. After spear harvest (mid-June), adults and larvae feed on the ferns, reducing leaf area for photosynthesis and thus carbohydrate storage in the roots. This effects spear width and abundance the next spring.

Cutworm (various species). Overwintering larvae from the family Noctuidae (primarily white cutworm) will feed on the tips and sides of developing spears in the early spring. Damaged spears display a "shepherd's crook" appearance, and are unmarketable for both fresh and processed uses. Black-sided cutworms overwinter as eggs, with the larvae feeding on asparagus spears from May through July.

Rust (*Puccinia asparagi*). This fungus is a pathogen of fern growth after spear harvest. Damage to the plant's root system occurs when ferns are attacked every year, resulting in a weakened crown. Over time, this results in unmarketable spears (too thin to meet production standards) or even plant death. Fungicides are applied to control this disease beginning 10-14 days after harvest.

Purple Spot (*Stemphyllium vesicarium*). Lesions from this fungus may appear on spears during harvest time, resulting in loss of marketable product. However, the greatest impact is on the ferns; repeated defoliation of fern growth can reduce plant vigor and subsequently yield. Fungicides are applied to control this disease beginning 10-14 days after harvest.

Pesticides Used

1. Chlorothalonil (Bravo)

Substituted aromatic, broad-spectrum foliage-protectant fungicide. Registered in Michigan as Section 18 only. Used on ferns to control purple spot.

- Oral LD₅₀ (rats) > 10,000 mg per kg body weight
Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight
“Fairly persistent” on crop surfaces. Half-life in aerobic soils 1-3 months.
100 day PHI (Section 18)
2. Mancozeb (Penncozeb, Dithane)
Used to control rust on ferns.
Oral LD₅₀ (rats) > 5000 mg per kg body weight
Dermal LD₅₀ (rabbits) > 8000 mg per kg body weight
Non- to moderately persistent (up to 18 months) in the environment.
180 day PHI
3. Carbaryl (Sevin)
Broad-spectrum, systemic, cholinesterase inhibitor, widest use of any insecticide. Used on spears to control adult common asparagus beetles to prevent egg contamination of marketable product.
Oral LD₅₀ (rats) = 307 mg per kg body weight
Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight
Insecticidal properties on crop for 3-10 days. Half life in aerobic soil 7 days, anaerobic 28 days.
1 day PHI
4. Chlorpyrifos (Lorsban)
Broad-spectrum, systemic organophosphate insecticide. Single pre-harvest application made to control cutworms when spears first emerge.
Oral LD₅₀ (rats) = 135 mg per kg body weight
Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight
Residues can remain on foliage for 10-14 days, with a soil half-life of 11-141 days.
1 day PHI

Materials and Methods—see Appendix A

Grower and Experimental spray application timelines—see Figure 1

Results and Discussion

The asparagus samples in this study, both from experimental and grower fields, as well as fresh and processed samples, were tested for 67 pesticides (Appendix B). Only carbaryl and chlorothalonil residues were detected, although the single latter detection was thought to have resulted from drift, not application to the asparagus crop. The only other pesticides used in this study were chlorpyrifos and mancozeb. Mancozeb was used for rust on the ferns in 1997, in both grower fields and in some of the experimental plots (Fig. 1); however, no residue was found on the spring 1998 samples (Table 2). Chlorpyrifos was applied once in the spring to control cutworms (Fig. 1), and residues of this product were not detected in the samples (Table 2).

Carbaryl is applied to asparagus spears in the spring for control of the common asparagus beetle (Fig. 1). The short pre-harvest interval of carbaryl is ideal for asparagus, since spears may be harvested daily, and there is zero tolerance for asparagus beetle eggs or feeding damage on raw or processed product. Since the samples were taken during the 1998 harvest season, carbaryl residues were possible. Carbaryl was detected on 49% of the asparagus samples, but all of the residues were well below the current federal tolerance (Table 3, Fig. 2).

In the samples from the research plots, carbaryl was found on more of the late samples, as well as in greater amounts, than on the early ones (Table 3). The converse was true for the grower samples. The processed samples contained no detectable residues of carbaryl (or any other pesticide for which analysis was performed). The multiple washings and heat treatment used in processing the product probably either removed the pesticides or broke them down.

Chlorothalonil was detected in only one bulked “late” sample (see Methods, Appendix A), from a grower’s farm. In an “early” sample from the same growers farm, chlorothalonil was not detected. When samples from individual harvest making up the initial bulked sample were tested separately (additional asparagus from each sample date had been reserved in a freezer), spears from only one of the dates tested positive for the chemical. This product is only applied to the ferns of asparagus, after the spear harvest season has ended and long before the next spring when spear harvest resumes (Fig. 1). The product does not persist over the winter, and would not be found on spears, confirmed by our data. This product is labeled for use on Douglas fir to control needle cast; the asparagus fields in question were surrounded by Christmas tree plantations. Consequently, the single sample that contained a detectable residue of chlorothalonil was thought to result from spray drift. Despite routine applications of chlorothalonil in some of the experimental treatments (Fig. 1), again, none was detected in the samples from the next spring.

References

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Table 1. Summary of Insecticides and Fungicides Registered for Use on Asparagus

Active Ingredient	Common Name	Type ¹	Active Ingredient	Common Name	Type ¹
<i>Used during 1997-1998²</i>			<i>Not used in 1997-1998²</i>		
permethrin	Ambush/Pounce	O	dimethoate	Cygon	OP
carbaryl	Sevin	Carb	disulfoton	Di-syston	OP
chlorothalonil	Bravo	B2	fenamiphos	Nemacur	OP
chlorpyrifos	Dursban/Lorsban	OP	lindane	Lindane	O
mancozeb	Penncozeb	B2	malathion	Cythion	OP
			methomyl	Lannate	Carb
			triadimefon	Bayleton	Other

¹ B2 = B2 carcinogen; Carb = carbamate; OP = organophosphate; Other = other category.

² Refers to pesticides used by Michigan growers in this study.

Table 2. Potential and actual product use in asparagus, 1997-1998, with pre-harvest intervals and residue found.

Product	<i>n</i> ^a	Maximum Rate ^b	Actual Total Use (rate X #app)		PHI ^c (days)	Actual PHI (days)		Tolerance (ppm)	Residue Results		
			Mean	Range		Mean	Range		No. (%) Positive Samples	Mean (ppm)	Range (ppm)
Grower (6)											
carbaryl	6	7.5 lb	1.27 lb	0.5-3.0	1	^d		10	6 (35)	0.08	BQL ^e -0.4
chlorothalonil	6	11 lb	4.8 lb	3.9-6.3	100	244	235-250	0.1	1 (6)	0.07	0.07
chlorpyrifos	3	2 pt	1 pt	0.3-2	1	23	16-27	5	0	--	--
EBDC	3	8.5 lb	2.8 lb	1.5-4.5	180	264	248-291	0.1	0	--	--
Experimental (5)											
carbaryl	5	7.5 lb	^f		1	^f		10	22 (55)	0.07	BQL-0.1
chlorothalonil	3	11 lb	7 lb	6-9	100	242	242	0.1	0	--	--
chlorpyrifos	5	2 pt	2 pt	2	1	4	4	5	0	--	--
EBDC	1	8.5 lb	12 lb	12	180	232	232	0.1	0	--	--

^aNumber of growers who recorded application of product during 1997-1998, or number of experimental plots to which product was applied.

^bBased on 1997/1998 product label.

^cLabeled pre-harvest interval, expressed in days.

^dMultiple harvests were taken during 1-3 applications of carbaryl, with minimum PHIs of 1 day.

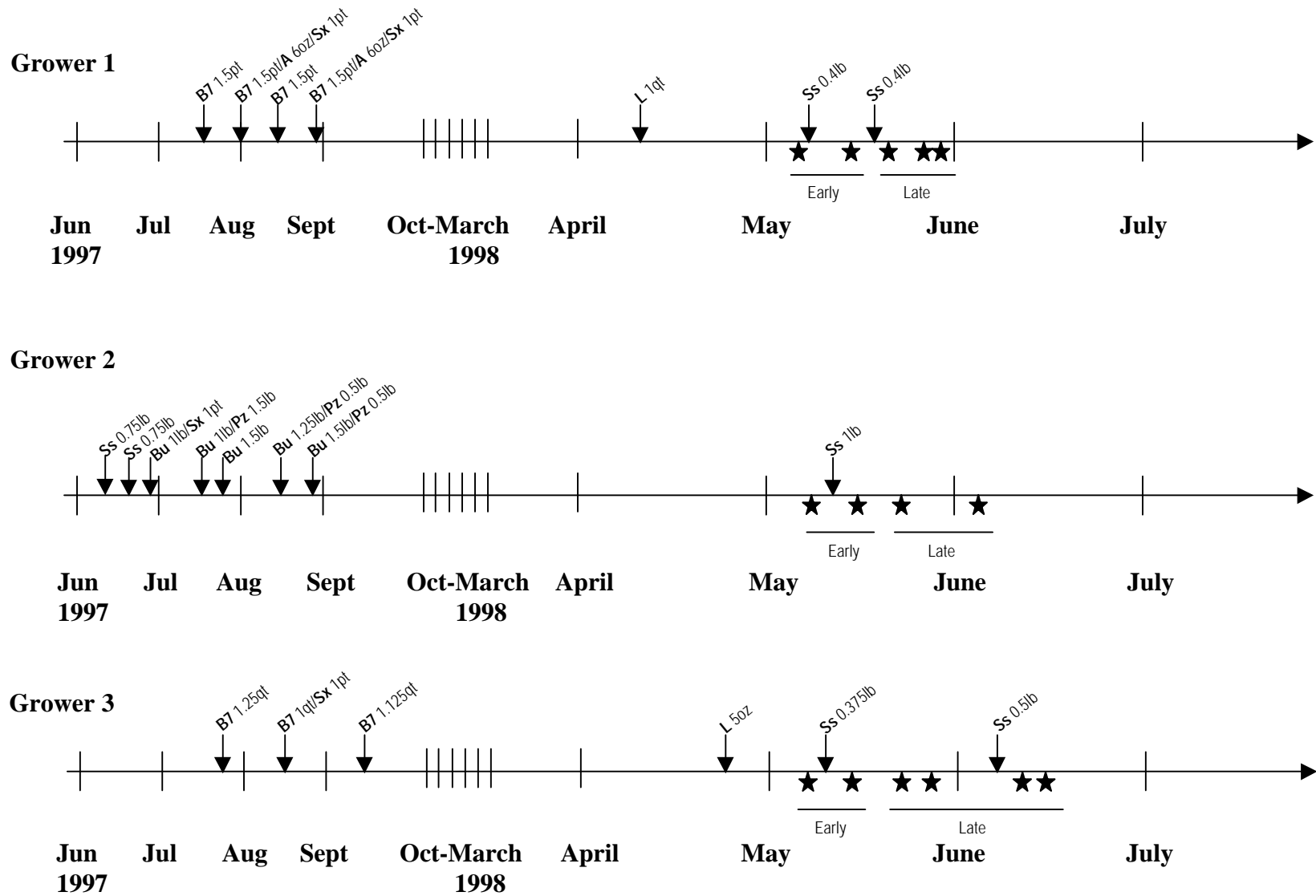
^eBQL: detected, but Below Quantifiable Limit.

^fResearch done on grower farm, carbaryl spray records not available.

Table 3. Summary of Carbaryl Residues on Asparagus; Tolerance = 10 ppm.

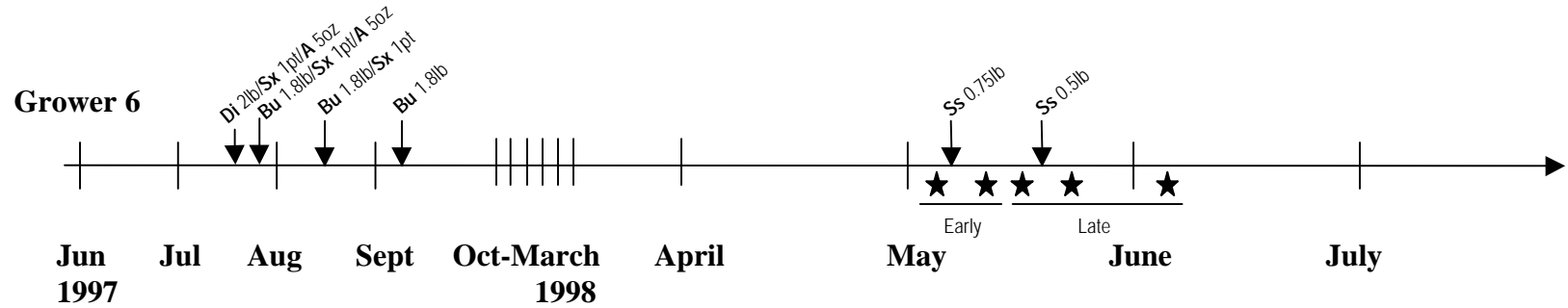
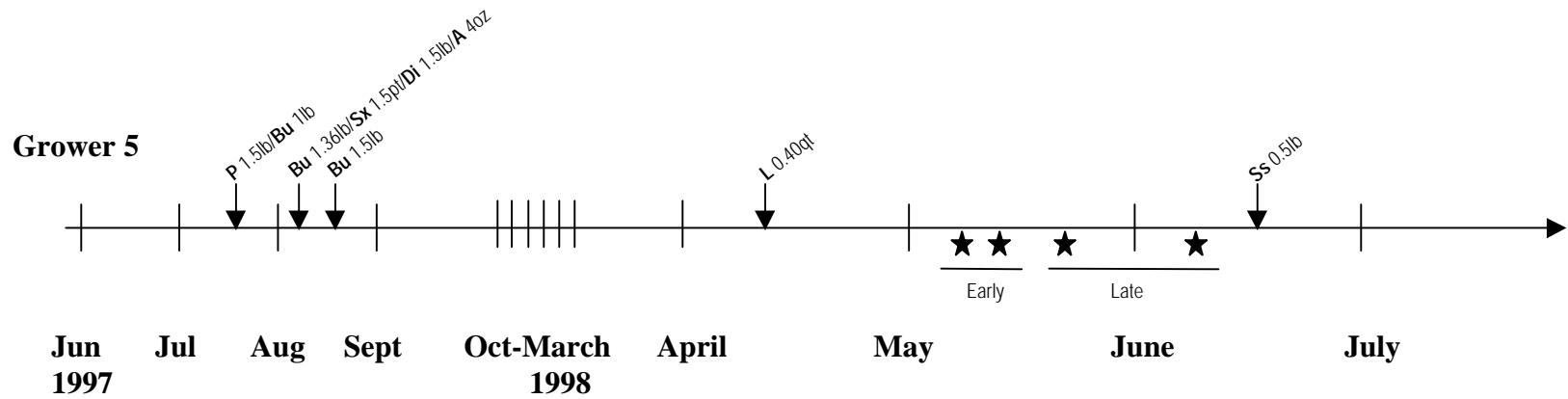
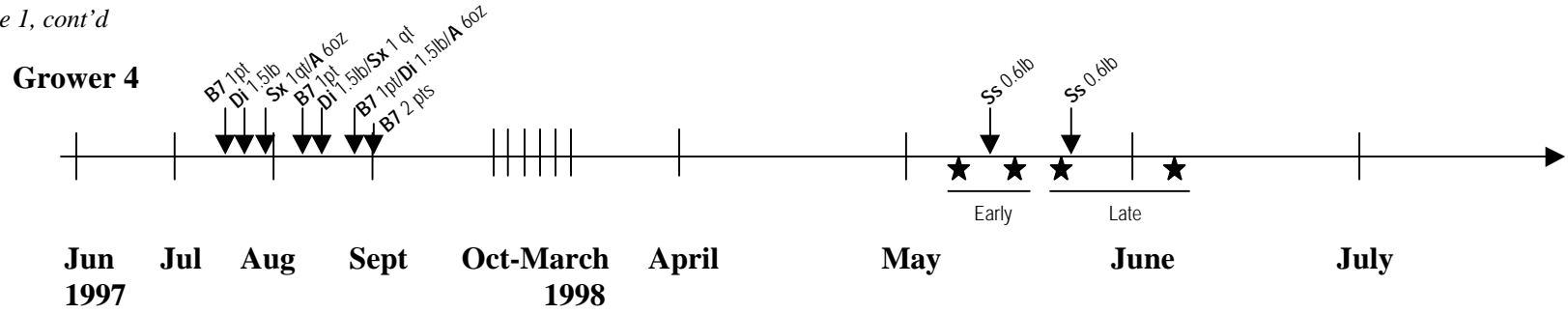
Description of samples	No. of samples tested	No. (%) Positive Samples	Range of residues (ppm)	Mean residue ± standard error (ppm)
All samples	57	28 (49)	BQL – 0.4	
Research samples	40	22 (55)	BQL – 0.1	0.06 (0.024)
Early	20	2 (10)	BQL – 0.07	0.036 (0.048)
Late	20	20 (100)	0.04-0.1	0.066 (0.005)
Grower samples	17	6 (35.3)	BQL - 0.4	0.078 (0.158)
Fresh	12	6 (50)		
Early	6	4 (66.7)	BQL-0.4	0.10 (0.199)
Late	6	2 (33.3)	BQL-0.04	0.03 (0.014)
Processed	5	0	--	--
Early	2	0	--	--
Late	3	0	--	--

Figure 1. Grower and experimental spray records for asparagus, 1997-1998



↓ = Pesticide Application. A = Ambush, Bu = Bravo Ultrex, B7 = Bravo 720, Di = Dithane, L = Lorsban 4E, P = Penncozeb 75DF, Sx = Sevin XLR, Ss = Sevin 80WSP. All product amounts per acre.
 ★ = Samples taken

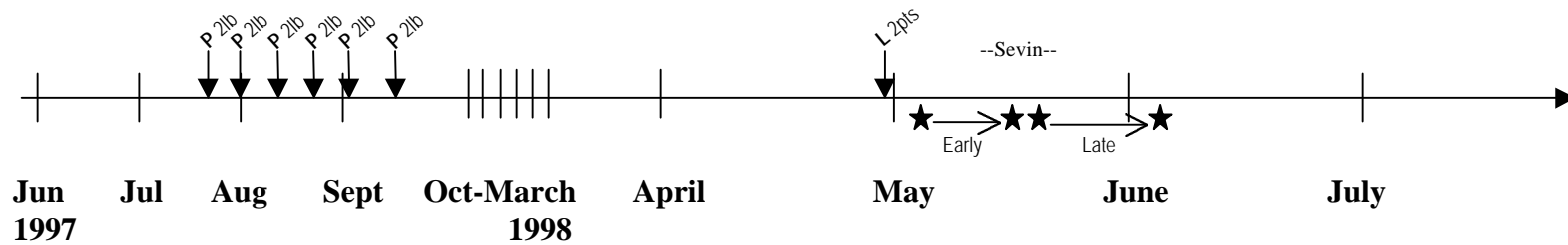
Figure 1, cont'd



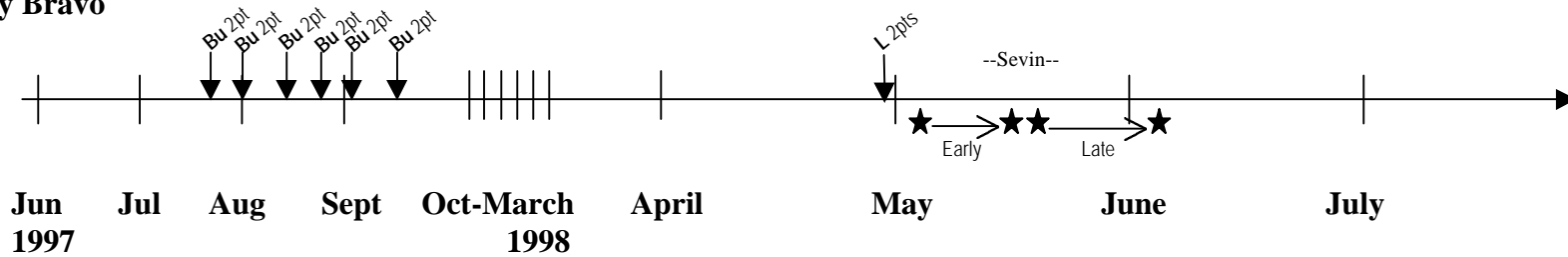
↓ = Pesticide Application. A = Ambush, Bu = Bravo Ultrex, B7 = Bravo 720, Di = Dithane, L = Lorsban 4E, P = Penncozeb 75DF, Sx = Sevin XLR, Ss = Sevin 80WSP. All product amounts per acre.
 ★ = Samples taken

Figure 1, cont'd

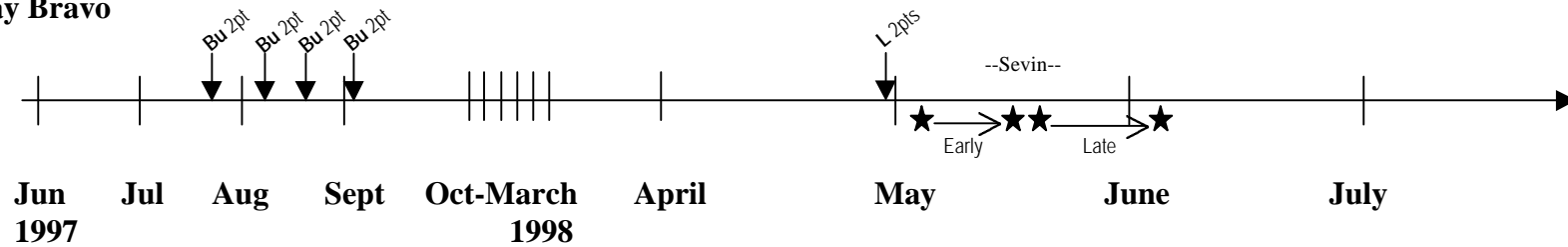
Experimental
10-day Penncozeb



10-day Bravo



14-day Bravo

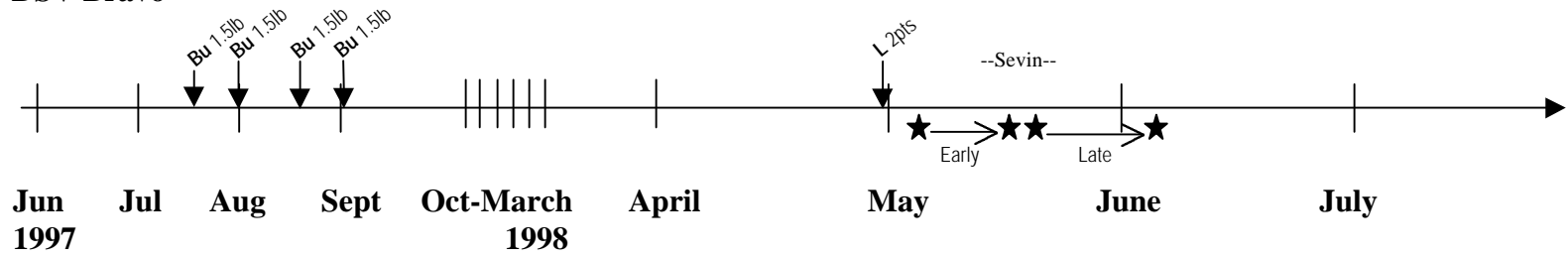


↓ = Pesticide Application. A = Ambush, Bu = Bravo Ultrex, B7 = Bravo 720, Di = Dithane, L = Lorsban 4E, P = Penncozeb 75DF, Sx = Sevin XLR, Ss = Sevin 80WSP. All product amounts per acre.
★ = Samples taken

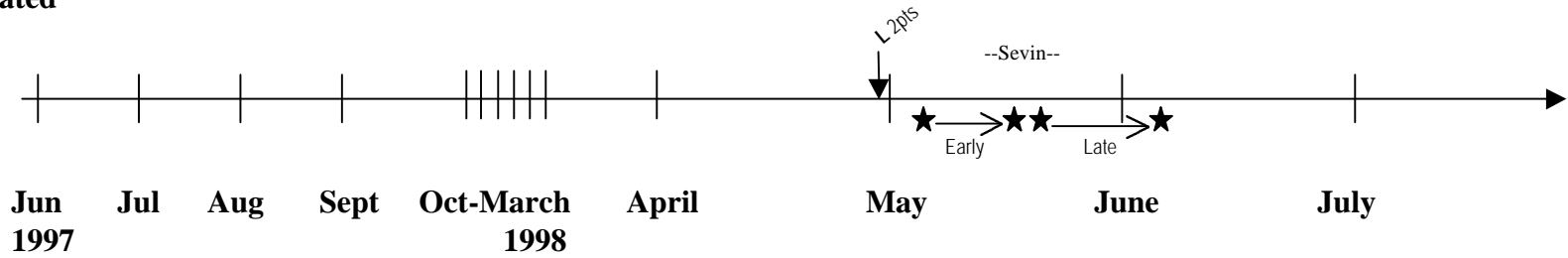
Figure 1, cont'd

Experimental cont'd

15-day DSV Bravo



Untreated



↓ = Pesticide Application. A = Ambush, Bu = Bravo Ultrex, B7 = Bravo 720, Di = Dithane, L = Lorsban 4E, P = Penncozeb 75DF, Sx = Sevin XLR, Ss = Sevin 80WSP. All product amounts per acre.
★ = Samples taken

Appendix A—Materials and Methods

Harvest and handling

A. Research samples

The research plots of asparagus were located in Oceana County, Michigan. During the fall of 1997, fungicide trials for the control of *Stemphylium* purple spot were conducted by Michigan State University. The plots consisted of two varieties: Jersey Giant and Jersey Knight. Five fungicide treatments were selected for this study, with four replicates of each treatment: (1) Bravo Weather Stik, 10-day spray schedule; (2) Bravo Weather Stik, 14-day spray schedule; (3) Bravo Weather Stik; TomCast 15 DSV model spray schedule (certain fungal diseases, such as *Stemphylium* purple spot of asparagus, are more likely to reach economically damaging levels after leaves have been wet at a certain temperature for a given amount of time. TomCast is a disease prediction model based on the duration of this period when fungal growth could occur, with the units referred to as Disease Severity Values [DSV]. In this treatment, fungicide sprays were applied when 15 DSV have been accumulated since the last fungicide application); (4) Penncozeb, 10-day spray schedule; (5) untreated control. The insecticide treatments were made by the grower cooperator, and were identical for all plots.

Spears were harvested the next spring, from each replicate of each treatment on 17 dates (4 May to 5 June 1998). The samples were individually stored in sealed plastic bags and were immediately placed in a freezer (10°F) until they were combined by date. The samples that were collected between 4 May and 17 May were grouped together as “early” samples, and the samples collected between 19 May and 5 June were grouped together as “late” samples. These composites were made for each of the five treatments and four replicates, for a total of 40 samples. The examination of early and late samples was to determine whether pesticide residues differed throughout the four-week asparagus harvest.

Combining protocol: Since asparagus harvests from the research plots were small (1-2 pounds each date), these samples were combined to obtain the minimum 10 pounds of product necessary for residue analysis. Each sample that was analyzed for pesticide residues was made up of a composite of 8 dates (“early”) or 9 dates (“late”) for each replicate of each treatment. A subsample of approximately 15 spears was taken from each date/treatment/replicate combination, and was placed in a plastic bag together with the other “early” or “late” dates for that treatment and replicate. The 40 combined samples were stored in the freezer (10°F) until residue analysis.

B. Grower samples – fresh:

Six asparagus growers participated in this study, from Oceana and Mason Counties, Michigan. Pesticides used and the timing of applications are in Figure 1.

Spears were harvested by each grower (Fig. 1), and within 24 hours of harvest, samples were collected from shipping crates on 4 – 6 dates (6 May to 9 June 1998). These samples were individually stored in sealed plastic bags and were immediately placed in a freezer (10°F) until they were combined by date. The samples that were collected between 6 May and 14 May were grouped together as “early” samples, and the samples collected between 18 May and 9 June were grouped together as “late” samples. These composites by the two dates were made for each of the six growers, for a total of 12 samples. This examination of early and late samples was to determine whether pesticide residues differed throughout the four-week asparagus harvest.

Combining protocol: As with the research samples, each sample that was analyzed for pesticide residues was made up of a composite of 2 – 3 dates (“early”) or 2 – 4 dates (“late”) for each replicate of each treatment. A subsample of spears was taken from each date/grower combination to total approximately 100 spears/sample. The spears were placed in a plastic bag together with the other “early” or “late” dates for that treatment and replicate. The 12 combined samples were stored in the freezer (10°F) until residue analysis.

C. Grower samples – processed

Three of the six asparagus growers described above also participated in the processing aspect of this study. All three growers were located in Oceana and Mason Counties, Michigan.

Spears were harvested by each grower on four dates between 8 May and 9 June 1998, and underwent hydrocooling within 24 hours of harvest. The spears were then kept in cold storage for 1 – 2 days until processing. During the canning process, the asparagus underwent four water washes. The canned samples (four per grower) were stored at room temperature until residue analysis. Like the fresh samples, these processed samples were composited by date. The samples that were collected between 6 May and 14 May 1998 were grouped together as “early” samples, and the samples collected between 23 May and 9 June 1998 were grouped together as “late” samples. These composites by the two dates were made for each of the three growers, with the exception of one

grower who only had “late” samples, for a total of five samples. This designation was made to determine whether pesticide residues differed throughout the four week asparagus harvest.

Combining protocol: Each sample that was analyzed for pesticide residues was made up of a composite of 1 – 3 dates (“early”) or 1 – 4 dates (“late”) for each replicate of each treatment. A subsample of cans (12 oz./can) was taken from each date/grower combination to total approximately four cans/sample. The cans were placed in a plastic bag together with the other “early” or “late” dates for that treatment and replicate, and the five composited samples were stored at room temperature until residue analysis.

Pesticide residue analysis.

Laboratory Division of the Michigan Department of Agriculture performed the residue analysis:

- I. The samples arrived in the laboratory frozen. They were stored in a freezer, then thawed prior to grinding and extraction. Preparation of the sample followed Section 102 of the Pesticide Analytical Manual (1997, Vol. 1, 3rd edition, U.S. Dept. of Health and Human Services, Public Health Service, Food and Drug Administration, pp.102-1—102-3). None of the samples were washed prior to analysis. The whole sample of asparagus was used after discarding any decomposed parts.
- II. The extraction method used for most of the compounds was the “Luke II modified Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods.” This is a modification of the “Acetone Extraction Screening Method for Pesticide Residues in Non-Fatty, High Moisture Foods,” (Pesticide Analytical Manual, 1997, Vol. I, Sect. 302, U.S. Dept. of Health and Human Services, Food and Drug Administration). This is a multi-residue method for the analysis of organohalogen, organonitrogen, organophosphate, organosulfur, and carbamate pesticide residues in nonfatty, high moisture matrices, and returns both quantitative and qualitative results. Analysis of all the compounds except the carbamates was by Gas Chromatography/Mass Spectroscopy (GC/MS). Analysis of the carbamates was by Liquid Chromatography/Post-Column Derivatization/Fluorescence Detection, with carbaryl confirmation by MS.
- III. The extraction and analysis method used for Benomyl was from “HPLC Fluorometric Analysis of Benomyl and Thiabendazole in Various Agricultural Commodities” (Bulletin #3650, E. J. Wojtowicz)
- IV. Dithiocarbamates were analyzed using the Lowen and Pease method (G. Zweig [Ed.], 1964. Analytical methods for Pesticides, Plant Growth Regulators, and Food Additives, p. 65. *In* Fungicides, Nematocides and Soil Fumigants, Rodenticides, and Food and Feed Additives, Vol. III, Academic Press).
- V. Limits of Detection were originally set by analyzing a set of spikes at or near the believed limit of detection. The standard deviation was determined and multiplied by the student’s T, at the 99% confidence level, to calculate the limit of detection. If the calculated limit of detection appeared excessively low or high, a set of spikes was analyzed at a level thought to be more realistic, based on the signal to noise ratio. If all of these new spikes were detected and confirmed, then this became the new limit of detection. These were determined in one commodity and then assumed to be the same in other commodities unless spike recovery data indicated otherwise.
- VI. Tolerances were from Duggan (1998, Pesticide Chemical News Guide, CRC Press LLC).

Appendix B—All pesticides included in the residue analysis of all asparagus samples.

Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)	Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)
3-Hydroxycarbofuran	M	0.002	none	Hexazinone	H	0.15	none
Acephate	I	0.63	none	Imazilil	F	2	none
Alachlor	H	0.019	none	Iprodione	I	0.065	none
Aldicarb	I	0.001	none	Lindane	I	0.063	1
Aldicarb Sulfone	M	0.002	none	Malathion	I	0.17	8
Aldicarb Sulfoxide	M	0.002	none	Methamidophos	I	0.30	none
Anilazine	F	0.15	none	Methidathion	I	0.055	none
Atrazine	H	0.025	none	Methomyl	I	0.002	2
Azinphos-Methyl	I	0.09	none	Methyl Parathion	I	0.058	none
Captan	F	0.075	none	Metolachlor	H	0.045	none
Carbaryl	I	0.002	10	Mevinphos	I	0.15	none
Carbofuran	I	0.001	none	Myclobutanil	F	0.14	none
Chlorothalonil	F	0.03	0.1 regional	Oxamyl	I	0.002	none
Chlorpropham	H	0.066	none	Oxyfluorfen	H	0.075	none
Chlorpyrifos	I	0.038	5 regional	p,p'-DDE	M	0.013	0.5 revoked
Cypermethrin	I	0.20	none	p,p'-DDT	I	0.013	0.5 revoked
DCPA	H	0.013	none	p,p'-Dicofol	I	0.22	none
Diazinon	I	0.016	none	Pendimethalin	H	0.035	none
Dichloran	F	0.050	none	Pentachlorobenzene	O	0.013	notfound
Dichlorvos	I	0.033	none	Pentachloronitrobenzene	F	0.030	none
Dieldrin	I	0.050	0.03 revoked	<i>cis</i> -Permethrin	I	0.028	1
Dimethoate	I	0.036	0.15 regional	<i>trans</i> -Permethrin	I	0.038	1
Diphenylamine	F	0.014	none	Phorate	I	0.042	none
Disulfoton	I	0.10	0.1 regional	Phosalone	I	0.045	none
Endosulfan I	I	0.050	none	Phosmet	I	0.044	none
Endosulfan II	I	0.060	none	Phosphamidon	I	0.28	none
Endosulfan Sulfate	M	0.075	none	Propargite	I	0.050	none
Ethion	I	0.011	none	Simazine	H	0.035	10
Ethoprop	I	0.035	none	Terbufos	I	0.025	none
Ethyl Parathion	I	0.055	none	Thiabendazole	F	2	none
Ethylenebis Dithiocarbamate	F	1	0.1 negligible	Triadimefon	F	0.17	0.15 regional
Fenamiphos	I	0.37	0.02 regional	Trifluralin	H	0.013	0.05
Fenvalerate	I	0.070	none	Vinclozolin	F	0.038	none
Hexachlorobenzene	F,I	0.023	not found				

^aF = Fungicide, H = Herbicide, I = Insecticide, M = Metabolite (break-down product), O = Other, *e.g.*, contaminant of the production process.

Blueberries

Introduction

Blueberry is a woody perennial in the heath family (Ericaceae), in the genus *Vaccinium*. Blueberry plants prefer acidic soils. Plants are propagated as stem or rhizome cuttings. Flowering begins in May, and fruit harvest is completed in August.

Michigan produces 44% of the U.S. total crop of blueberries. About 83% of Michigan blueberries are grown in Van Buren, Ottawa, and Allegan counties. The total acreage of blueberries by the end of 1997 was 17,000 acres, up 3 % from the previous year. The state produced 76 million pounds of blueberries (4,470 lbs/acre), with 28% going to fresh market and the remainder processed (canned, frozen, other products). At 99 cents/lb fresh and 59 cents/lb processed, the total farm-gate value of blueberry production in Michigan was \$53,198,000 in 1997.

Major Pests

Blueberry Maggot (*Rhagoletis mendax*). Pupae overwinter in the soil, with adults emerging from late June to September. The adult fly lays eggs in the ripening fruit. The maggots feed on the inside of the fruit, completely consuming the berry. Berries infested by larvae are difficult to separate from uninfested berries during harvest and packing, and maggots may emerge from the berries at the point of sale. FDA inspects interstate shipments of blueberries, and will seize and condemn any shipments containing even a single maggot. Consequently, blueberry maggot is often the most important insect pest of blueberries in some regions.

Cranberry Fruitworm (*Acrobasis vaccinii*). Adults lay eggs on early fruit-set berries, with larvae often entering fruit before full petal fall. Larvae generally move from berry to berry, welding a cluster together. Damage can be extensive, since egg laying continues for nearly a month.

Cherry Fruitworm (*Grapholita packardii*). Similar to cranberry fruitworm, except larvae spend their entire lifecycle in one or two berries.

Oblique-Banded Leafroller (*Choristoneura rosaceana*). Larvae feed on the developing fruit and foliage. Larvae overwinter and moths emerge during June, laying eggs on the leaves. The second generation feeds actively on fruit and foliage. Oblique-banded leafroller resistance to organophosphate insecticides is increasing in parts of Michigan.

Japanese Beetle (*Popillia japonica*). This beetle chews leaf tissue between the veins (skeletonizing), causing defoliation, browning, and leaf drop. Fruits may also be attacked. It is difficult to separate all of the beetles from infested fruit at harvest and during packing.

Mummy Berry (*Monilinia vacciniicorymbosi*). Mummy berry can cause severe crop losses of blueberries. The first symptoms appear as drooping leaves and shoots, followed by browning within one day. Vegetative tissues are generally killed within 24-72 hours after the first disease symptoms appear. Infected blossoms result in a dry fruit rot, causing the berries to mummify. These mummified berries (pseudosclerotia) may provide a source of inoculum (in or on the soil) for infection for several years. The severity of the disease depends on inoculum level, environmental conditions, and cultivar susceptibility.

Fusicoccum Canker (*Fusicoccum putrefaciens*). Infection begins with lesions on first- and second-year stems, which turn red by winter. The disease progresses the following spring, with the lesions coalescing to form a reddish-brown canker 1-10 cm long. In summer, leaves on

stems with cankers wilt; in severe infections, the plant can die. Primarily a disease of the highbush blueberry, when severe, this disease can significantly limit production.

Phomopsis Canker (*Phomopsis vaccinii*). This disease causes cankers on one- to three-year-old stems. The brownish canker may encircle the entire stem, with the surface of older cankers usually covered by pycnidia (fungal fruiting bodies). The canker usually progresses downward until the entire shoot is infected. During the summer, infected shoots with fruit may wilt. As little as 3.8 mm of rain in Michigan triggers the release of conidia (spores). Conidia are released from blossom bud swell through late August during each rain event. Reduced yields result from loss of viable flowers and buds on infected stems.

Anthracnose Fruit Rot (*Colletotrichum gloeosporioides*). Also called “ripe rot”, anthracnose causes the fruit to rot as they near maturity. The ripe fruit softens and sunken spots appear on the fruit, which may then become covered with salmon-colored conidia. The fungus can also cause lesions on the leaves. Losses in Michigan may range from 10 to 20%, although post-harvest losses can be much more severe. Symptoms first appear on the blossoms. The fungus overwinters in infected stems. Yield losses are greatest when weather conditions favor disease development (long periods of warm, wet weather) from bloom until harvest.

Phytophthora Root Rot (*Phytophthora cinnamomi*). Phytophthora primarily invades the feeder roots of blueberry plants, causing stunting of the entire plant. Infection by this fungus can be quite rapid, with the fungus invading the vascular tissue of the roots within 24 hours. The development of the disease is worse on poorly drained soils.

Botrytis Blight (*Botrytis cinerea*). Botrytis commonly affects many crops around the world, including blueberry. Young, developing plant tissue, such as blossoms, leaves, shoots, and fruit are most susceptible. Botrytis can cause severe damage, particularly when environmental conditions are favorable (high humidity, >95%; and moderate temperatures, 59 – 68 F). Vegetative portions of the plant can be damaged, with yield reduction by the destruction of flowers and berries.

Pesticides Used

1. Azinphosmethyl (Guthion)

Non-systemic, broad-spectrum organophosphate insecticide, used to control blueberry tip borer, oblique-banded leafroller, cranberry fruitworm, cherry fruitworm, and blueberry maggot.

Oral LD₅₀ (rats) = 5 mg per kg body weight

Dermal LD₅₀ (rabbits) = 220 mg per kg body weight

Persistence in soil dependent upon soil type, ranging from 30-days to 1-year breakdown time.

On vegetation, the approximate residual period is 1-3 weeks

7 day PHI.

2. Carbaryl (Sevin)

Broad-spectrum, systemic, cholinesterase inhibitor, widest use of any insecticide; introduced in 1956. Used to control oblique-banded leafroller, Japanese beetle, and fruitworms.

Oral LD₅₀ (rats) = 307 mg per kg body weight

Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Insecticidal properties on crop for 3-10 days. Half life in aerobic soil 7 days, anaerobic 28 days.

0 day PHI

3. Malathion (Cythion)

A non-systemic aliphatic organophosphate used for control oblique-banded leafroller, fruitworms, Japanese beetle, and blueberry maggot.

Oral LD₅₀ (rats) = 885 mg per kg body weight

Dermal LD₅₀ (rabbits) > 4,000 mg per kg body weight

Soil degradation is rapid. The average half-life is 6 days. Increased moisture content increases degradation.

0-1 day PHI

4. Phosmet (Imidan)

Non-systemic, organophosphate insecticide. Used to control blueberry maggot, leafrollers, Japanese beetle, and cherry fruit fly.

Oral LD₅₀ (rats) = 147 mg per kg body weight

Dermal LD₅₀ (rabbits) = 3160 mg per kg body weight

Half-life in sandy loam soil 3-19 days, with increasing rates of breakdown in higher pH.

3 day PHI

5. Benomyl (Benlate)

A systemic fungicide with a wide spectrum of activity, controlling canker, anthracnose, and fruit rots.

Oral LD₅₀ (rats) > 10,000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight

Benomyl is strongly bound to soil. The half-life is 6-12 months.

21 day PHI

6. Captan

Non-systemic sulfenimide fungicide, used to control mummy berry, fusisocum canker, phomopsis canker, anthracnose, and alternaria fruit rots.

Oral LD₅₀ (rats) = 9000 mg per kg body weight

No dermal irritation

Half-life in soil 1-10 days, with activity on potato foliage for 23 days.

0 day PHI

7. Chlorothalonil (Bravo)

Substituted aromatic, broad-spectrum foliage-protectant fungicide. Used to control phomopsis canker, anthracnose, and alternaria fruit rots.

Oral LD₅₀ (rats) > 10,000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight

“Fairly persistent” on crop surfaces. Half-life in aerobic soils 1-3 months

21 day PHI

8. Fosetyl-Al (Aliette)

Systemic organophosphate fungicide, used to control Phytophthora and downy mildews.

Oral LD₅₀ (rats) = 5800 mg per kg body weight

Dermal LD₅₀ (rabbits) > 3200 mg per kg body weight

0 day PHI

9. Triflorine (Funginex)

A systemic fungicide that controls several fungal diseases, such as mummy berry.

Oral LD₅₀ (rats) > 16,000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight

Materials and Methods—see Appendix A

Grower and Experimental spray application timelines—see Figure 1

Results and Discussion

A total of four blueberry samples were examined for residues, three from commercial farms and one from an MSU research plot. All samples were tested for a total of 65 pesticides and metabolites (Appendix B). Three different pesticides were detected.

The three growers in this survey used most of the products labeled for use on blueberries (Table 1, Fig. 1), though usually at significantly lower total application rates than the labels allow (Table 2). Although all growers did apply organophosphates, either azinphos-methyl, malathion, or phosmet (Fig. 1), no organophosphates were detected in the residue analysis (Table 2).

Captan was detected in two of the grower samples (Table 2), although spray records indicate that captan was only applied by Grower #3 (Fig. 1). Since captan is not a Restricted Use Pesticide, growers are not necessarily required to record applications. Captan was also detected in the experimental sample, where it had been applied five times (Fig. 1).

Both chlorothalonil and carbaryl were detected only in Grower #1's samples, the only grower who applied these products. In both cases, the residue was 100- (chlorothalonil) to 1000-fold (carbaryl) less than current tolerance (Table 2). There were no residues detected for the additional pesticides listed in Appendix B.

Grower #1 also applied DiPel early in the season (Fig. 1), probably to control one of the Lepidopteran insect pests such as the oblique-banded leafroller. *Bacillus thuringiensis* is specific to caterpillars and has no vertebrate toxicity, but must be applied when larvae are small as well as applied frequently for optimal control.

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Table 1. Summary of Insecticides and Fungicides Registered for Use on Blueberries

Common Name	Trade name	Type ¹	Common Name	Trade name	Type ¹
<i>Used during 1998</i> ²			<i>Not used in 1998</i> ²		
azinphos-methyl	Guthion	OP	metalaxyl	Ridomil	O
<i>B.thuringiensis</i>	Various names	O	methomyl	Lannate	Carb
benomyl	Benlate	Carb			
captan	Captan	O			
carbaryl	Sevin	Carb			
chlorothalonil	Bravo	B2			
fosetyl-AI	Aliette	OP			
malathion	Malathion	OP			
phosmet	Imidan	OP			
terbacil	Sinbar	O			
triflorine	Funginex	O			

¹ B2 = B2 carcinogen; Carb = carbamate; OP = organophosphate; OC = organochlorine; O = other category.

² Refers to pesticides used by Michigan growers in this study.

Table 2. Potential and actual product use in blueberries, 1998, with pre-harvest intervals and residue found.

Product	n ^a	Maximum Rate ^b	Actual Total Used		PHI ^c (days)	Actual PHI		Tolerance (ppm)	Residue Results		
			(rate X #app)			(days)			No. (%) Positive Samples	Mean (ppm)	Range (ppm)
Grower (3)											
captan	1	70 lb	10 lb	--	0	34	--	25	2 (67)	0.53	0.06-1
carbaryl	1	12.5 lb	2 lb	--	7	31	--	10	1 (33)	0.01	--
chlorothalonil	1		8 pt	--	Bloom	88	--	1	1 (33)	0.01	--
phosmet	2	-- ^d	1.8 lb	1-2.66	3	14	13-15	10	0	--	--
malathion	2	-- ^d	2 pt	2	1	22	13-31	8	0	--	--
azinphos-methyl	2	-- ^d	2.4 lb	2-2.8	7	42	34-60	5	0	--	--
Experimental (1)											
captan	1	70 lb	25 lb	25	1	48	48	25	1 (100)	0.2	0.2

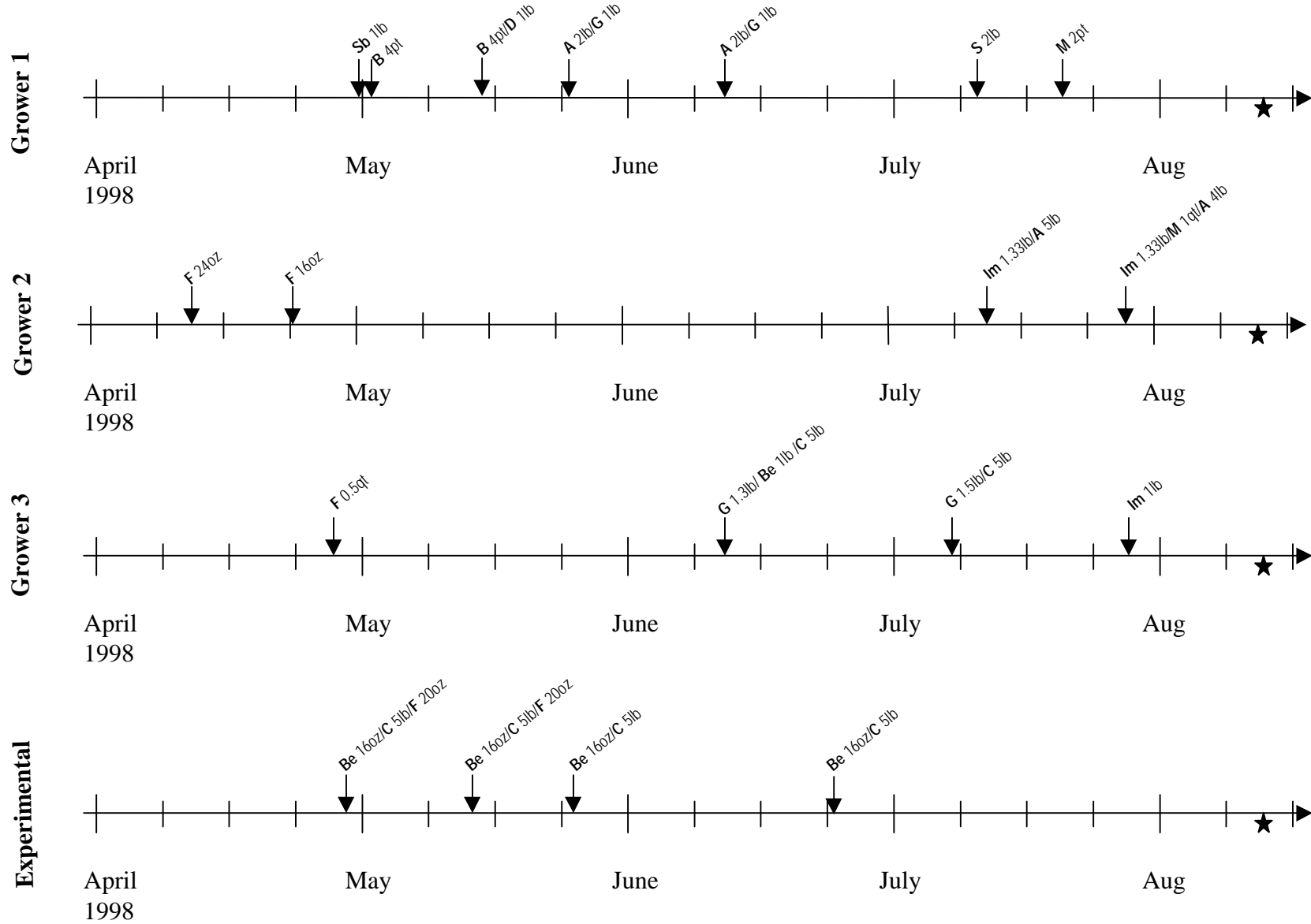
^aNumber of growers who recorded application of product during 1998, or number of experimental plots to which product was applied.

^bBased on 1998 product label.

^cLabeled pre-harvest interval, expressed in days.

^dNo maximum use restriction on 1998 label.

Figure 1. Grower and experimental spray records for blueberries, 1998.



↓ = Pesticide application. A = Aliette, B = Bravo, Be = Benlate, C = Captan, D = DiPel, F = Funginex, G = Guthion, Im = Imidan, M = Malathion, S = Sevin, Sb = Sinbar. All product amounts per acre.
 ★ = Samples taken

Appendix A – Materials and Methods

Harvest and handling

A. Research samples

The research plot of blueberries (variety ‘Elliott’) was located at the Southwest Michigan Research and Extension Center (SWMREC) in Van Buren County, Michigan. SWMREC staff conducted horticultural trials for increased fruit yield during the 1998 growing season. Pesticides used and the timing of applications are in Figure 1 (note that there was no control of blueberry maggot, for which nearly all commercial growers treat). Approximately 10 lbs. of blueberries were harvested by hand from the bushes on 10 August 1998. The fruit was placed in a plastic bag and then stored in the freezer (10°F) until residue analysis.

B. Grower samples – fresh:

Three Michigan blueberry growers participated in this study. The samples from Growers #1 and #3 were var. ‘Jersey’, and the sample from Grower #2 was var. ‘Elliott’. Pesticides used and the timing of applications are in Figure 1. Approximately 10 lbs. of blueberries per grower were harvested by hand on 10 August 1998. Each sample was stored as described above.

Pesticide Residue Analysis

The Laboratory Division of the Michigan Department of Agriculture performed the residue analysis. All samples were delivered to the laboratory on 2 September 1998.

- I. The samples arrived in the laboratory frozen. They were stored in a freezer, then thawed prior to grinding and extraction.
- II. Preparation of the sample followed Section 102 of the Pesticide Analytical Manual (PAM) Vol. 1 (pp.102-1—102-3). None of the samples were washed prior to analysis. For blueberries, the whole commodity was used after discarding stems.
- III. The extraction method used for most of the compounds was the “Luke II modified Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods.” This is a modification of the “Acetone Extraction Screening Method for Pesticide Residues in Non-Fatty, High Moisture Foods,” (Pesticide Analytical Manual, Vol. I, Sect. 302, U.S. Department of Health and Human Services, Food and Drug Administration). This is a multi-residue method for the analysis of organohalogen, organonitrogen, organophosphate, organosulfur, and carbamate pesticide residues in nonfatty, high moisture matrices, and returns both quantitative and qualitative results. Analysis of all the compounds except the carbamates was by Gas Chromatography/Mass Spectroscopy (GC/MS). Analysis of the carbamates was by Liquid Chromatography/Post-Column Derivatization/Fluorescence Detection, with carbaryl confirmation by MS.
- IV. The extraction and analysis method used for Benomyl was from “HPLC Fluorometric Analysis of Benomyl and Thiabendazole in Various Agricultural Commodities” (Bulletin #3650, E. J. Wojtowicz).
- V. Dithiocarbamates were analyzed using the Lowen and Pease method (G. Zweig [Ed.], 1964. Analytical methods for Pesticides, Plant Growth Regulators, and Food Additives, p. 65. *In* Fungicides, Nematocides and Soil Fumigants, Rodenticides, and Food and Feed Additives, Vol. III, Academic Press).
- VI. Limits of Detection were originally set by analyzing a set of spikes at or near the believed limit of detection. The standard deviation was determined and multiplied by the student’s T, at the 99% confidence level, to calculate the limit of detection. If the calculated limit of detection appeared excessively low or high, a set of spikes was analyzed at a level thought to be more realistic, based on the signal to noise ratio. If all of these new spikes were detected and confirmed, then this became the new limit of detection. These were determined in one commodity and then assumed to be the same in other commodities unless spike recovery data indicated otherwise.
- VII. Tolerances were from Duggan (1998, Pesticide Chemical News Guide, CRC Press LLC).

Appendix B—All pesticides included in the residue analysis of all blueberry samples

Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)	Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)
3-Hydroxycarbofuran	M	0.002	none	Hexachlorobenzene	F,I	0.023	not found
Acephate	I	0.63	none	Imazilil	F	2	none
Alachlor	H	0.019	none	Iprodione	F	0.065	15
Aldicarb	I	0.001	none	Lindane	I	0.063	none
Aldicarb Sulfone	M	0.002	none	Linuron	I	0.078	none
Aldicarb Sulfoxide	M	0.002	none	Malathion	I	0.17	8
Anilazine	F	0.15	10	Methamidophos	I	0.30	none
Atrazine	H	0.025	none	Methidathion	I	0.045	none
Azinphos-Methyl	I	0.09	5	Methomyl	I	0.002	6
Benomyl	F	0.06	7	Methyl Parathion	I	0.058	1
Captan	F	0.075	25	Metolachlor	H	0.045	none
Carbaryl	I	0.002	10	Mevinphos	I	0.15	none
Carbofuran	I	0.001	none	Myclobutanil	F	0.14	1 regional
Chlorothalonil	F	0.005	1.0	Oxamyl	I	0.002	none
Chlorpropham	H	0.066	0.3 interim	Oxyfluorfen	H	0.045	none
Chlorpyrifos	I	0.038	2	p,p'-DDE	M	0.013	0.1 revoked
Cypermethrin	I	0.20	none	p,p'-DDT	I	0.013	0.1 revoked
DCPA	H	0.013	none	p,p'-Dicofol	I	0.22	none
Diazinon	I	0.016	0.5	Pendimethalin	H	0.035	none
Dichloran	F	0.050	none	Pentachlorobenzene	O	0.013	not found
Dichlorvos	I	0.033	none	Pentachloronitrobenzene	F	0.030	none
Dieldrin	I	0.050	none	<i>cis</i> -Permethrin	I	0.028	none
Diphenylamine	F	0.014	none	<i>trans</i> -Permethrin	I	0.038	none
Disulfoton	I	0.10	none	Phosalone	I	0.045	none
Endosulfan I	I	0.050	0,1	Phosmet	I	0.044	10
Endosulfan II	I	0.060	0.1	Phosphamidon	I	0.28	none
Endosulfan Sulfate	M	0.075	0.1	Propargite	I	0.050	none
Ethion	I	0.011	none	Simazine	H	0.035	0.25
Ethoprop	I	0.035	none	Terbufos	I	0.025	none
Ethyl Parathion	I	0.055	1	Thiabendazole	I	2	none
Fenamiphos	I	0.2	none	Triadimefon	I	0.17	none
Fenvalerate	I	0.070	3	Trifluralin	H	0.013	none
Hexazinone	H	0.15	0.2	Vinclozolin	F	0.038	none

^aF = Fungicide, H = Herbicide, I = Insecticide, M = Metabolite (break-down product), O = Other, *e.g.*, contaminant of the production process.

Cucumbers

Introduction

Cucumber (*Cucumis sativus*) is a warm-season annual plant in the family Cucurbitaceae, which includes squash, melon, and watermelon. Plants are direct-seeded into fields. Cucumber plants are monoecious, requiring the presence of, and pollen from, male plants. The primary pollinators are bees, which are essential for fruit set and yield. Harvest for processing (pickles) occurs one time in the season, when all fruits are picked then graded for processing. Fresh-market harvests are repetitive, occurring every 2-4 days.

In Michigan, a total of 30,600 acres of cucumbers were harvested in 1997, with most (82%), of the acreage devoted to processing for pickles. Total 1997 value of Michigan cucumbers was \$35.6 million, which was a 7% decrease from 1996.

Major Pests

Striped cucumber beetle (*Acalymma vittatum*). This leaf-feeding beetle can cause damage to cucurbits in two ways. The first is direct damage from feeding, by decreasing leaf area and thus photosynthesis of the plant. Significant defoliation can decrease yield. Beetle larvae feed on the roots, which can kill seedlings. More importantly, the striped cucumber beetle is the vector for *Erwinia tracheiphila*, the causative agent of bacterial wilt. This disease can cause 100% loss of some squash varieties. There is no treatment for this infectious disease except removal of infected plants.

Seed maggot (*Hylemya platura*). The larvae of this fly bore into either the seed or the germinating sprout, and can thus significantly reduce plant stand through plant death.

Powdery mildew (*Erysiphe cichoracearum*). This fungus attacks all cucurbits, causing a white, powdery growth on leaves, which may wilt and die. Loss of photosynthesis may decrease fruit production.

Downy mildew (*Pseudoperonospora cubensis*). The disease causes yellow to brown spots on leaves, which develop into purplish mildew under humid conditions. As the spots spread, the leaves die, again reducing fruit yield.

Fruit rot (*Phytophthora capsici*). In addition to fruit rot, this species is the causative agent for crown rot, damping off, and foliar blight. The fungus overwinters in the soil. This disease can infect stored fruit, so if symptoms of the disease appear in the field, growers will often abandon the entire field.

Alternaria fruit spot (*Alternaria cucumerina*). The fungus overwinters in seed and field debris. Lesions can ultimately cause leaf defoliation. In addition, the fungus readily grows on the fruit and can spread to rot the entire cucumber while it is in storage.

Pesticides Used

There was minimal insect or disease pressure during the growing season of 1998. Therefore, it was believed that no insecticides or fungicides were applied prior to sampling.

Materials and Methods

Harvest and handling

Grower samples – fresh:

Two Michigan pickle growers participated in this study. Pesticide usage data is not available from these growers at this time, but was believed that the growers did not apply any insecticides or fungicides. Approximately 5 lbs. of pickling cucumbers were sampled from each grower at

the processor in late August and September. The samples were taken immediately after harvest, and were placed in a plastic bag and stored in the freezer (10°F) until residue analysis.

Pesticide Residue Analysis

The Laboratory Division of the Michigan Department of Agriculture performed the residue analysis.

- I. The samples arrived in the laboratory frozen, 1 Sept. 1998. They were stored in a freezer, then thawed prior to grinding and extraction. Preparation of the sample followed Section 102 of the Pesticide Analytical Manual (1997, Vol. 1, 3rd edition, U.S. Dept. of Health and Human Services, Public Health Service, Food and Drug Administration, pp.102-1—102-3). None of the samples were washed prior to analysis. The whole sample was used after discarding stems.
- II. The extraction method used for most of the compounds was the “Luke II modified Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods.” This is a modification of the “Acetone Extraction Screening Method for Pesticide Residues in Non-Fatty, High Moisture Foods,” (Pesticide Analytical Manual, 1997, Vol. I, Sect. 302, U.S. Dept. of Health and Human Services, Food and Drug Administration). This is a multi-residue method for the analysis of organohalogen, organonitrogen, organophosphate, organosulfur, and carbamate pesticide residues in nonfatty, high moisture matrices, and returns both quantitative and qualitative results. Analysis of all the compounds except the carbamates was by Gas Chromatography/Mass Spectroscopy (GC/MS). Analysis of the carbamates was by Liquid Chromatography/Post-Column Derivatization/Fluorescence Detection, with carbaryl confirmation by MS.
- III. The extraction and analysis method used for Benomyl was from “HPLC Fluorometric Analysis of Benomyl and Thiabendazole in Various Agricultural Commodities” (Bulletin #3650, E. J. Wojtowicz)
- IV. Dithiocarbamates were analyzed using the Lowen and Pease method (G. Zweig [Ed.], 1964. Analytical methods for Pesticides, Plant Growth Regulators, and Food Additives, p. 65. *In* Fungicides, Nematocides and Soil Fumigants, Rodenticides, and Food and Feed Additives, Vol. III, Academic Press).
- V. Limits of Detection were originally set by analyzing a set of spikes at or near the believed limit of detection. The standard deviation was determined and multiplied by the student’s T, at the 99% confidence level, to calculate the limit of detection. If the calculated limit of detection appeared excessively low or high, a set of spikes was analyzed at a level thought to be more realistic, based on the signal to noise ratio. If all of these new spikes were detected and confirmed, then this became the new limit of detection. These were determined in one commodity and then assumed to be the same in other commodities unless spike recovery data indicated otherwise.
- VI. Tolerances were from Duggan (1998, Pesticide Chemical News Guide, CRC Press LLC).
- VII. All cucumber samples were tested for the pesticides listed in Appendix A.

Results and Discussion

While there are a number of insect and disease pathogens that attack cucumbers, during the growing season of 1998, pest pressure was so low that few or no insecticides or fungicides were applied. Consequently, it was not surprising that there were no pesticide residues detected, from the list in Appendix A. The findings from this year highlight the fact that not all pesticides registered (see Table 1) for a crop are used, nor are they necessarily used at the maximum rate allowed or used until the labeled pre-harvest interval.

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Table 1. Summary of Insecticides and Fungicides Registered for Use on Cucumbers.

Common Name	Trade name	Type ¹	Common Name	Trade name	Type ¹
<i>Labeled but not used during 1998²</i>			carbofuran	Furadan	Carb
carbaryl	Sevin, Adios	Carb	chlorothalonil	Bravo	B2
fosetyl-Al	Aliette	OP	metalaxyl	Ridomil	O
azinphos-methyl	Guthion	OP	methomyl	Lannate	Carb
esfenvalerate	Dithane	O	EBDC	Manzate, Dithane, Pencozeb	B2
copper	Kocide	O	captan	Captan	O
benomyl	Benlate	Carb	endosulfan	Asana, Thiodan	O
triflorine	Funginex	O	thiophanate methyl	Topsin	B2
carbophenothion	Trithion	OP	dicofol	Kelthane	OC
malathion	Malathion	OP	diazinon	Diazinon	OP

¹ B2 = B2 carcinogen; Carb = carbamate; OP = organophosphate; OC = Organochlorine; O = other category.

² Refers to pesticide use by this sample of Michigan growers.

Appendix A. All pesticides included in the residue analysis of all cucumber samples.

Compound	Type ^a	Limit of Detection	Tolerance	Compound	Type ^a	Limit of Detection	Tolerance
		(ppm)	(ppm)			(ppm)	(ppm)
3-Hydroxycarbofuran	M	0.002	0.4	Imazilil	F	2	none
Acephate	I	0.63	none	Iprodione	I	0.065	none
Alachlor	H	0.019	none	Lindane	I	0.063	3
Aldicarb	I	0.001	none	Linuron	H	0.078	none
Aldicarb Sulfone	M	0.002	none	Malathion	I	0.17	8
Aldicarb Sulfoxide	M	0.002	none	Methamidophos	I	0.30	1.0
Anilazine	F	0.15	10	Methidathion	I	0.055	none
Atrazine	H	0.025	none	Methomyl	I	0.002	0.2 negligible
Azinphos-Methyl	I	0.09	2.0	Methyl Parathion	I	0.058	1
Benomyl	F	0.06	1.0	Metolachlor	H	0.045	none
Captan	F	0.075	25	Mevinphos	I	0.15	0.2
Carbaryl	I	0.002	10	Myclobutanil	F	0.14	0.5 pending
Carbofuran	I	0.001	0.4	Omethoate	I	0.17	none
Chlorothalonil	F	0.005	5	Oxamyl	I	0.002	2.0
Chlorpropham	H	0.066	none	Oxyfluorfen	H	0.045	none
Chlorpyrifos	I	0.038	0.05	p,p'-DDE	M	0.013	0.1 revoked
Cypermethrin	I	0.20	none	p,p'-DDT	I	0.013	0.1 revoked
DCPA	H	0.013	1	p,p'-Dicofol	I	0.22	5
Diazinon	I	0.016	0.75	Pendimethalin	H	0.035	none
Dichloran	F	0.050	5	Pentachlorobenzene	O	0.013	not found
Dichlorvos	I	0.033	0.5	Pentachloronitrobenzene	O	0.030	none
Dieldrin	I	0.050	0.1	<i>cis</i> -Permethrin	I	0.028	none
Dimethoate	I	0.036	none	<i>trans</i> -Permethrin	I	0.038	none
Diphenylamine	F	0.07	none	Phorate	I	0.042	none
Endosulfan I	I	0.050	2.0	Phosalone	I	0.045	none
Endosulfan II	I	0.060	2.0	Phosmet	I	0.044	none
Endosulfan Sulfate	M	0.075	2.0	Phosphamidon	I	0.28	0.5
Ethion	I	0.011	0.5	Propargite	I	0.050	none
Ethoprop	I	0.035	0.02 negligible	Simazine	H	0.035	none
Ethyl Parathion	I	0.055	1	Terbufos	I	0.025	none
Fenamiphos	I	0.2	none	Thiabendazole	F	2	none
Fenvalerate	I	0.070	0.5	Triadimefon	F	0.17	0.3
Hexachlorobenzene	F,I	0.023	not found	Trifluralin	H	0.013	0.05 negligible
Hexazinone	H	0.15	none	Vinclozolin	F	0.038	none

^aF = Fungicide, H = Herbicide, I = Insecticide, M = Metabolite (break-down product), O = Other, *e.g.*, contaminant of the production process.

Grapes

Introduction

Grapes are classified in the family Vitaceae, and are woody perennial vines. Grapevines are grown from rooted cuttings or from grafts on rootstock. Depending on cultivar, berry growth to maturity can take as much as 100 days in the Great Lakes region.

Michigan is the fourth largest producer of grapes in the United States. Total production of grapes decreased 6%, to 61,000 tons in 1997. Of this, 45,600 tons were 'Concord' grapes and 13,400 tons were 'Niagara'. Berrien and Van Buren counties are the top two grape producing counties in Michigan, accounting for 88% of the total acreage. The amount of grapes produced for the fresh market was down from 1996, to 200 tons; grapes for juice were up to 58,200 tons, as was usage for wine production, to 2,600 tons. The total farm-gate value of grape production in Michigan was over \$15 million in 1997.

Although Concord and Niagara comprise the largest acreage of grapes in Michigan, several additional cultivars are grown for wine production. Grape cultivars differ in their susceptibility to several of the important diseases. Concord and Niagara are susceptible to some degree to all of the diseases summarized below.

Major Pests

Grape Berry Moth (*Endopiza viteana*). The moth overwinters as a pupa, with adults emerging the first week of June. There can be up to three generations per year in lower Michigan. The first generation larvae feed on foliage and small fruit. In subsequent generations, larvae tunnel directly into the fruit, feeding on pulp and seeds. Damaged fruit shrivel and fall, and may lead to loss of most of the crop. Grapes also may be webbed together and sticky with juice. Grape berry moth damage tends to predispose fruit to bunch rot problems at harvest, exacerbating potential crop losses. In addition to chemical control, mating disruption can be a useful strategy to help manage this pest.

Grape Leafhopper (*Erythroneura comes*). Grapevines can tolerate relatively high populations (6 to 15 grape leafhoppers per leaf) with little or no economic damage (the threshold varies by time of the season, crop load, vine condition, etc.). However, heavy leafhopper feeding can result in premature leaf drop, lowered sugar content, increased acid, and poor color of the fruit. Ripening grapes can be covered with sticky insect excrement, which also allows for growth of sooty mold. Also, severely infested vines may be unable to produce sufficient wood the following season. Damage to the vine can be serious if infestations are allowed to persist unchecked for two or more years.

Potato Leafhopper (*Empoasca fabae*). Potato leafhoppers are also periodic pests of grapes. This insect can cause significant leaf malformation and loss of photosynthetically functional leaf area. No practical economic thresholds have been developed for this insect pest on grape. Damage can be very serious on young vines or on heavily cropped vines. Potential reductions in fruit quality and vine winter hardiness are also possible.

Japanese Beetle (*Popillia japonica*). This beetle feeds on leaf tissue between the veins causing leaves to take on a skeletonized appearance, browning, and finally dropping off the vine. Fruits may also be attacked, causing yield reductions.

Climbing Cutworm. Multiple species of cutworms (Family Noctuidae) feed on grapes. They are sporadic pests that are mainly a serious problem of young plantings, where they may completely strip the buds and emerging foliage in the spring. Careful monitoring of populations,

vine phenology, and temperature can help reduce spray applications in some vineyards, in some years. Spot treatments can also be useful in some vineyards, in some years.

Rose Chafer (*Macrodactylus subspinosus*). This voracious beetle in the scarab family will feed on flowers, leaves, and fruit. The larvae feed on grass roots. While the adults will feed on many fruit, vegetable, and ornamental plants, grape remains among the most severely injured crops. While populations fluctuate from year to year, severe infestations can destroy large numbers of blossoms on a vine. Young vines can be severely injured by adult beetles.

Mites. There are many species of mites that may infest grapes including spider mites, grape rust mites, and European red mites. The symptoms vary but include yellowing and necrosis of leaves (called “mite-firing” in severe cases), abnormal vine growth, bud mortality, shortened internodes, and reduced fruit production.

Black Rot (*Guignardia bidwellii*). Symptoms of fungal infection include small, tan leaf spots that develop into black-ringed lesions. Severe infections can cause a significant loss of leaf area, as well as serving as a source of inoculum for later fruit infections. Lesions may also develop on petioles and may kill the entire leaf. Infected grapes eventually shrivel into unmarketable “mummies.” The fungus overwinters in these mummified berries on the soil or in old clusters still hanging from the vine, requiring free water to germinate.

Downy Mildew (*Plasmopara viticola*). This fungus attacks all green parts of the vine, especially the leaves, creating yellowish, oily lesions on the upper leaf surface, with downy white mats of fungus on the lower leaf surface. Severe infection causes defoliation of leaves with a potential decrease in fruit yield, fruit quality, and vine winter hardiness. *P. viticola* primarily overwinters as spores in fallen leaves, with better winter survival in moist soil. Spores germinate in water in the next spring, when splashing rain disperses the infective spores onto the new leaves.

Phomopsis Cane and Leaf Spot (*Phomopsis viticola*). Symptoms of fungal infection are small, angular, necrotic lesions on leaves in spring, which later elongate, and become brownish to purplish lesions on canes, tendrils, petioles, and cluster stems. Infected leaves serve as inoculum for fruit rot late in the season. In some years fruit falls off the clusters ahead of the harvester; fruit losses can be significant.

Powdery Mildew (*Uncinula necator*). This disease appears as a dusting of powdery white fungal mats covering leaves and fruit. The disease can reduce leaf area, and may impact yield and fruit quality by directly infecting the fruit. This fungus reduces vine growth and yield, and may impact winter-hardiness of the vine. If uncontrolled when environmental conditions are favorable for disease development, losses can be severe.

Botrytis Bunch Rot (*Botrytis cinerea*). Susceptibility to botrytis varies by cultivar. The fungus infects buds and shoots in early spring, then infects blooming flowers. Fruit are infected through wounds and can quickly rot, particularly in compact clusters and under dense foliage. Losses can be severe. Grapes damaged by insects (*i.e.*, grape berry moth) or disease (*i.e.*, powdery mildew) are especially susceptible to infection by botrytis.

Pesticides Used

1. Azinphos-methyl (Guthion)

Non-systemic, broad-spectrum organophosphate insecticide used to control grape berry moth and grape leafhopper.

Oral LD₅₀ (rats) = 5 mg per kg body weight

Dermal LD₅₀ (rabbits) = 220 mg per kg body weight

On vegetation, the approximate residual period is 1-3 weeks

10 day PHI

2. Carbaryl (Sevin)

Broad-spectrum, systemic, cholinesterase inhibitor, widest use of any insecticide. Used to control grape leafhopper, rose chafer, and Japanese beetle.

Oral LD₅₀ (rats) = 307 mg per kg body weight

Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Insecticidal properties on crop for 3-10 days. Half life in aerobic soil 7d, anaerobic 28 days.

7 day PHI

3. Methyl Parathion (Penncap-M)

Non-systemic, broad-spectrum organophosphate insecticide used to control grape berry moth, leafhoppers, Japanese beetle, and rose chafer.

Oral LD₅₀ (rats) = 270 mg per kg body weight

Dermal LD₅₀ (rabbits) = 5450 mg per kg body weight

On vegetation, the approximate residual period is 1-3 weeks

14 day PHI

4. Chlorpyrifos (Lorsban)

This is a heterocyclic organophosphate contact insecticide. Used in Michigan under a "Special Local Need" label to control climbing cutworm.

Oral LD₅₀ (rats) = 135 mg per kg body weight

Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Moderately persistent but relatively immobile. The half-life ranges from 11-141 days depending on soil type, soil pH, and aerobic conditions.

5. Dicofol (Kelthane)

This is an organochlorine used to control mites.

Oral LD₅₀ (rats) = 575 mg per kg body weight

Dermal LD₅₀ (rabbits) = 4000 mg per kg body weight

Insoluble in water and binds strongly to soil particles. Soil half-life is 60 days.

7 day PHI

6. Imidacloprid (Provado)

A systemic, chloro-nicotinyl insecticide with soil, seed, and foliar uses for the control of sucking insects; used in grapes to control leafhoppers.

Oral LD₅₀ (rats) = 450 mg per kg body weight

No dermal toxicity

Half-life of imidacloprid in soil is 48-190 days, depending on the amount of ground cover.

0 day PHI

7. Methomyl (Lannate)

A systemic carbamate insecticide used to control grape berry moth, grape leafhopper, and climbing cutworm.

Oral LD₅₀ (rats) = 17 mg per kg body weight

Dermal LD₅₀ (rabbits) = 1000 mg per kg body weight

The dissipation half-life is 3-6 weeks in soil. It is highly soluble in water, increasing the chances for ground water contamination.

14 day PHI for processed grapes, 1 day PHI for fresh grapes.

8. Phosmet (Imidan)
Non-systemic, organophosphate insecticide. Used to control grape berry moth and grape leafhopper.
Oral LD₅₀ (rats) = 147 mg per kg body weight
Dermal LD₅₀ (rabbits) = 3160 mg per kg body weight
Half-life in sandy loam soil 3-19 days, with increasing rates of breakdown in higher pH.
7 day PHI
9. Azoxystrobin (Abound)
A broad spectrum fungicide with both preventative and curative properties, used to control black rot, downy mildew, phomopsis cane and leaf spot, and powdery mildew.
Oral LD₅₀ (rats) > 5000 mg per kg body weight
Dermal LD₅₀ (rabbits) > 2000 mg per kg body weight
14 day PHI
10. Captan
Non-systemic broad spectrum fungicide used to control downy mildew, black rot, and phomopsis. Has some activity against botrytis, but no activity against powdery mildew.
Oral LD₅₀ (rats) = 9000 mg per kg body weight
No dermal toxicity
Half-life in soil 1-10 days
14 day PHI
11. Copper (Kocide, Champ, COCS)
Used as copper sulfate with lime and as copper hydroxide; protectant fungicide for black rot, downy mildew, and powdery mildew.
Oral LD₅₀ (rats) = 300 (sulfate) or 1000 (hydroxide) mg per kg body weight
Dermal irritant
No PHI restrictions if applied per label instructions
12. Dimethyldithiocarbamate (Ferbam)
Non-systemic fungicide used to control black rot and downy mildew.
Oral LD₅₀ (rats) > 4000 mg per kg body weight
No dermal toxicity
7 day PHI
13. Iprodione (Rovral)
Fungicide used to control botrytis bunch rot.
Oral LD₅₀ (rats) > 3500 mg per kg body weight
Dermal LD₅₀ (rabbits) > 2000 mg per kg body weight
7 day PHI
14. Mancozeb (Penncozeb, Manzate)
Non-systemic fungicide used to control black rot, downy mildew, and phomopsis cane and leaf spot.
Oral LD₅₀ (rats) > 8000 mg per kg body weight
No dermal toxicity
66 day PHI
15. Myclobutanil (Nova)
Systemic fungicide, both curative and protectant, used to control black rot and powdery mildew.

Oral LD₅₀ (rats) = 1600 mg per kg body weight

Dermal LD₅₀ (rabbits) > 5000 mg per kg body weight

14 day PHI

16. Triadimefon (Bayleton)

Systemic fungicide with protective and curative properties, for control of powdery mildew and black rot.

Oral LD₅₀ (rats) = 363 mg per kg body weight

Dermal LD₅₀ (rabbits) > 1000 mg per kg body weight

14 day PHI

17. Ziram

Non-systemic dithiocarbamate fungicide used to control powdery mildew.

Oral LD₅₀ (rats) = 1400 mg per kg body weight

Dermal LD₅₀ (rabbits) > 6000 mg per kg body weight

In the air and soil Ziram is readily degraded by ultraviolet light. Biodegradation may be slow due to the toxicity to bacteria.

21 day PHI

Materials and Methods—see Appendix A

Grower and Experimental spray application timelines—see Figure 1.

Results

A total of 20 grape samples were examined for residues, from 15 commercial vineyards. Ten samples came from standard commercial vineyards. Ten other samples came from on-farm research plots, five plots treated conventionally, and five others using pheromone disruption for grape berry moth control. All samples were tested for a total of 67 pesticides and metabolites (Appendix B). Four different pesticides were detected (Table 2).

The 15 growers in this study did not use all the products labeled for grapes (Table 1, Fig.1), nor did they use products at the maximum allowable rate per acre per season (Table 2). In addition, observed pre-harvest intervals were much longer than the label allowed (Table 2).

The organophosphates phosmet, azinphos-methyl, and methyl parathion were used by several growers. However, there were positive detections for these products on less than 15% of the samples tested, with no detection of azinphos-methyl despite its use by four growers (Table 2, Fig. 1). For phosmet, the mean residue was 27-fold less than the current federal tolerance. For methyl parathion, used by 11 growers, residue was found on only one sample, 2.5-fold less than tolerance (Table 2).

The carbamates methomyl and carbaryl were applied to control grape berry moth, grape leafhopper, and climbing cutworm. Although the PHI for both (on fresh grapes) is only one day, the growers who used these products did not apply them any closer than 40 days before harvest (Table 2). The mean detected residue was 125-fold and 250-fold less than tolerance for methomyl and carbaryl, respectively (Table 2). The use of pheromone disruption did decrease the use of carbaryl by Grower #8 (Fig. 1).

Although every grower used EBDC fungicides on every plot (Fig. 1, Table 2), there were no residues detected in any sample (Table 2). The amount of product applied ranged from 1-12 lbs per acre, with a minimal PHI of 109 days. The labeled PHI is from 7 days (Ferbam) to 66 days (Manzate and Pencozeb).

The organochlorine dicofol was used by one grower to control mites, but with a 99-day PHI, no residue of this product was detected in that sample. Finally, there were no residues detected for the additional pesticides listed in Appendix B.

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Table 1. Summary of Insecticides and Fungicides Registered for Use on Grapes.

Common Name	Trade Name	Type ¹	Common Name	Trade Name	Type ¹
<i>Used during 1998²</i>			<i>Labeled but not used in 1998²</i>		
azinphos-methyl	Guthion	OP	metalaxyl	Ridomil	O
azoxystrobin	Abound	O	benomyl	Benlate	O
captan	Captan	O	spectracide	Diazinon	OP
dithiocarbamate	Ferbam	B2	fenbutatin-oxide	Vendex	O
carbaryl	Sevin	Carb	endosulfan	Thiodan	OC
chlorpyrifos	Lorsban	OP	triflumizole	Procure	O
copper sulfate	Champ, Kocide	O	fenarimol	Rubigan	O
dicofol	Kelthane	OC	<i>Bacillus thuringiensis</i>	DiPel	O
imidacloprid	Provado	O	sulfur	Sulfur, Thiolux	O
iprodione	Rovral	O			
mancozeb	Penncozeb, Manex, Manzate,	B2			
methomyl	Lannate	Carb			
methyl parathion	Penncap-M	OP			
myclobutanil	Nova	O			
phosmet	Imidan	OP			
triadimefon	Bayleton	O			
ziram	Ziram				

¹ B2 = B2 carcinogen; Carb = carbamate; OP = organophosphate; OC = Organochlorine; O = other category.

² Refers to pesticides used by Michigan growers in this study.

Table 2. Potential and actual product use in grapes, 1998, with pre-harvest intervals and residue found.

Product	<i>n</i> ^a	Maximum Rate ^b	Actual Total Use (rate X #app)		PHI ^c (days)	Actual PHI (days)		Tolerance (ppm)	Residue Results		
			Mean	Range		Mean	Range		No. (%) Positive Samples	Mean (ppm)	Range (ppm)
Grower (15 standard + 5 pheromone)											
phosmet	1	-- ^d	1.5 lb	--	14	35	--	10	3 (15)	0.37	0.2-0.7
carbaryl	10	10 qt	1.7 qt	1-3	7	68	42-104	10	9 (45)	0.04	BQL ^e -0.3
methyl parathion	11	24 qt	2.2 qt	1-3	40	76	49-114	1	1 (5)	0.2	--
azinphos-methyl	4	6 lb	1.25 lb	1-2	10	52	23-99	5	0	--	--
methomyl	7	4.5 lb	0.61 lb	0.5-1	1 fresh 14 wine	63	44-80	5	3 (15)	0.04	BQL-0.05
EBDC	18	25.6 lb ^f	7.7 lb	1-12	66	116	109-124	variable	0	--	--

^aNumber of growers who recorded application of product during 1998.

^bBased on 1998 product label.

^cLabeled pre-harvest interval in days.

^dNo maximum rate restriction on 1998 label.

^eBQL, below quantifiable limit.

^fFrom Penncozeb 75DF label.

Figure 1. Grower spray records for grapes, 1998.

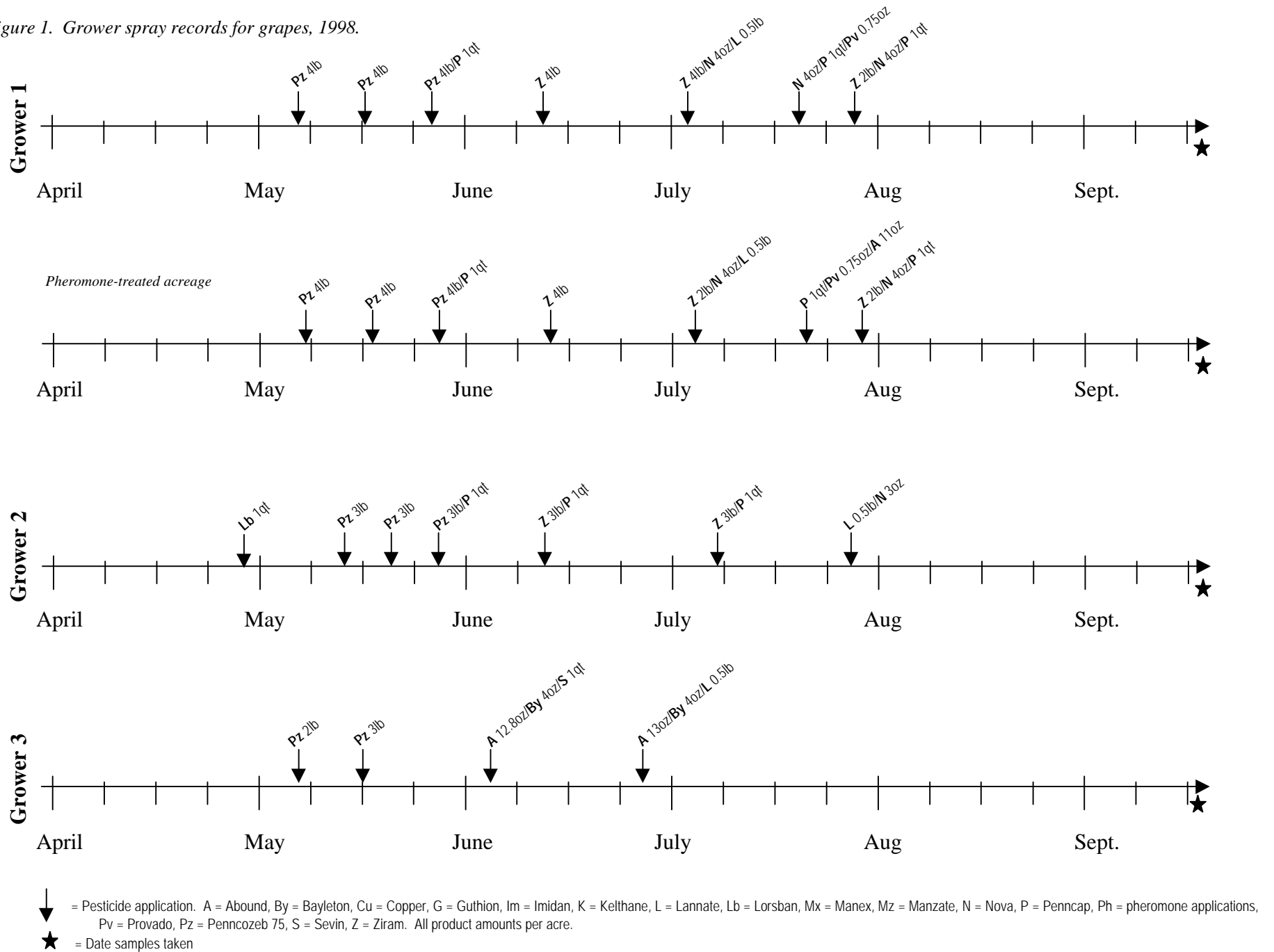
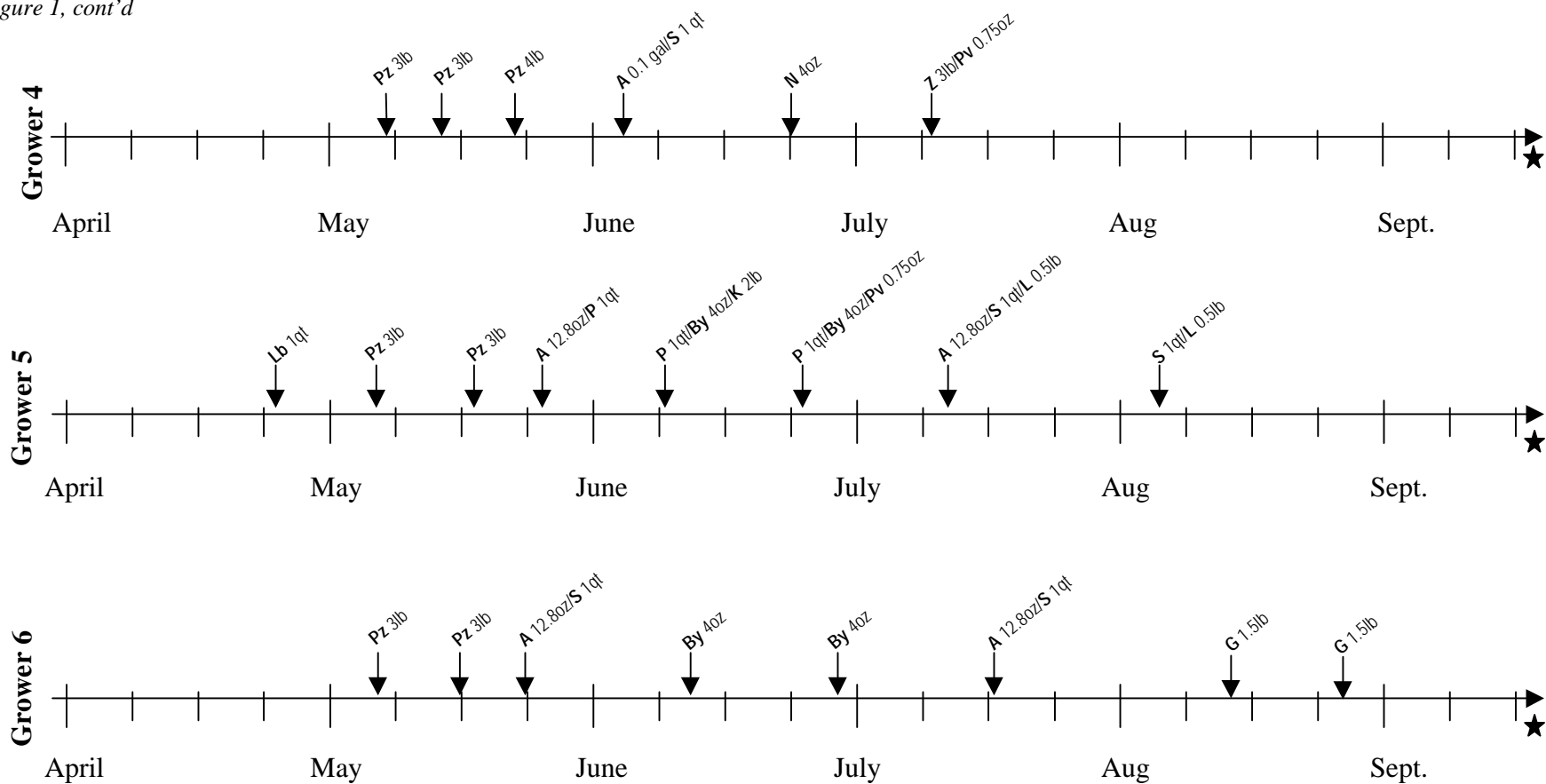
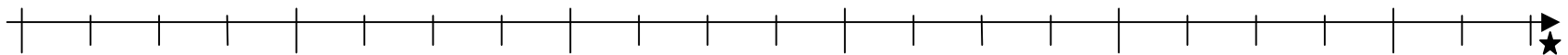


Figure 1, cont'd



Pheromone-treated acreage

Spray records not available



↓ = Pesticide application. A = Abound, By = Bayleton, Cu = Copper, G = Guthion, Im = Imidan, K = Kelthane, L = Lannate, Lb = Lorsban, Mx = Manex, Mz = Manzate, N = Nova, P = Penncap, Ph = pheromone applications, Pv = Provado, Pz = Penncozebe 75, S = Sevin, Z = Ziram. All product amounts per acre.
 ★ = Date samples taken

Figure 1, cont'd

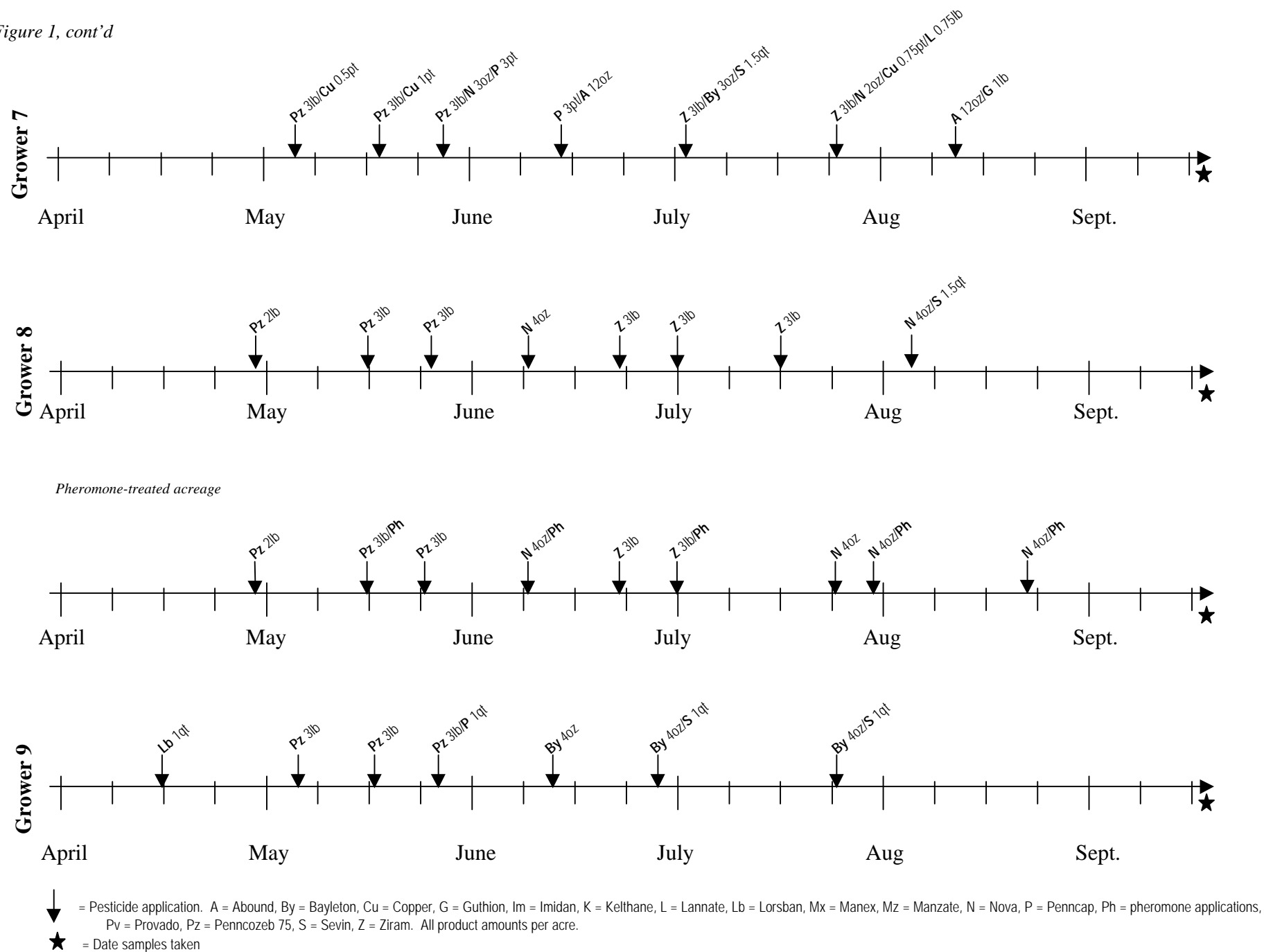
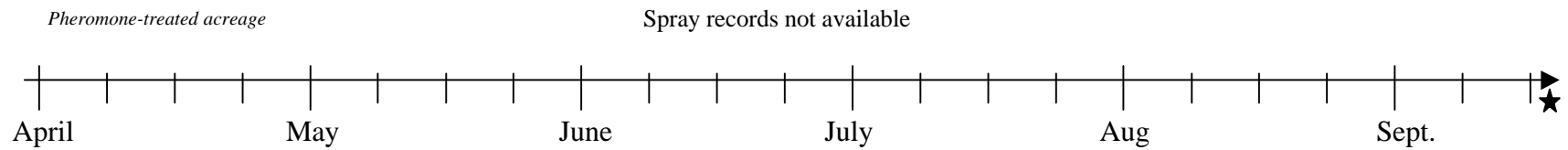
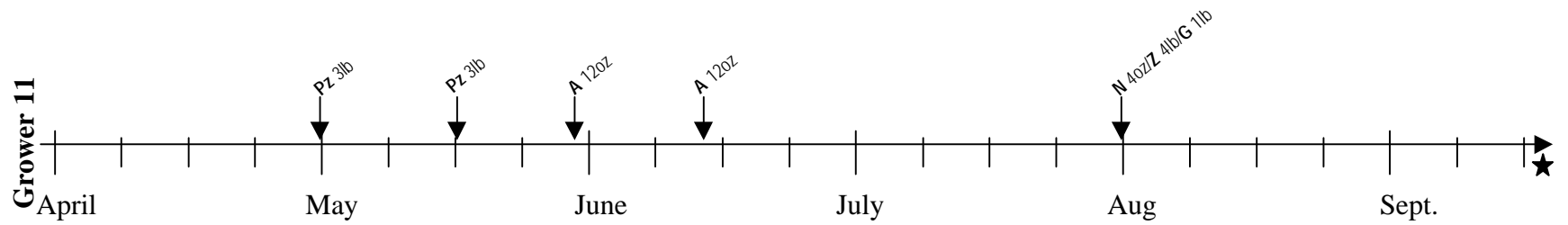
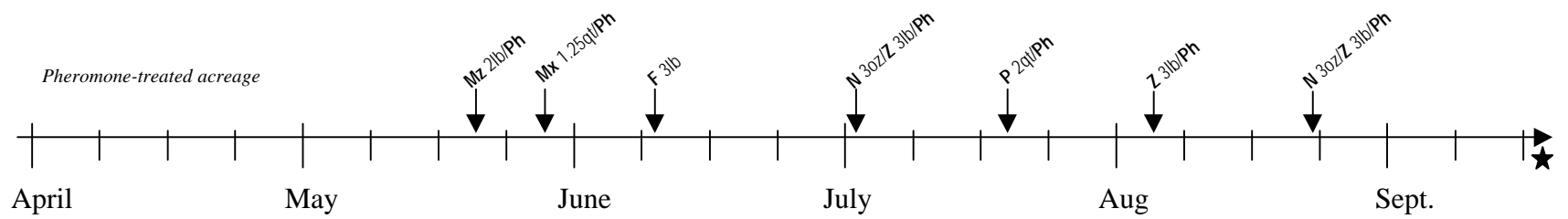
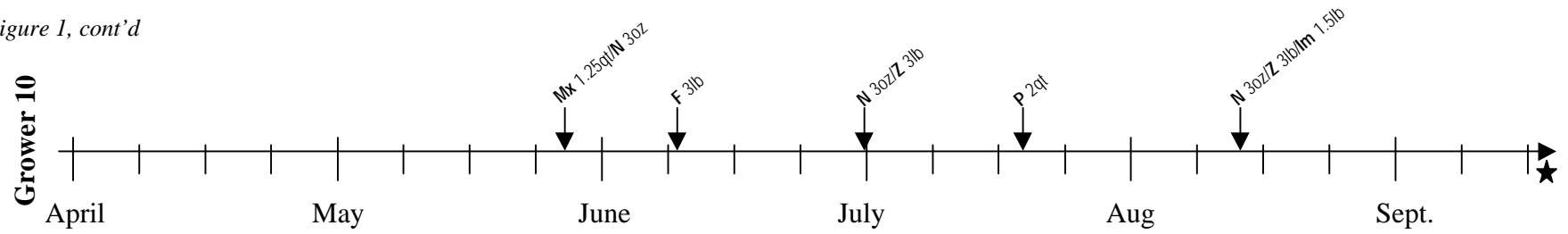
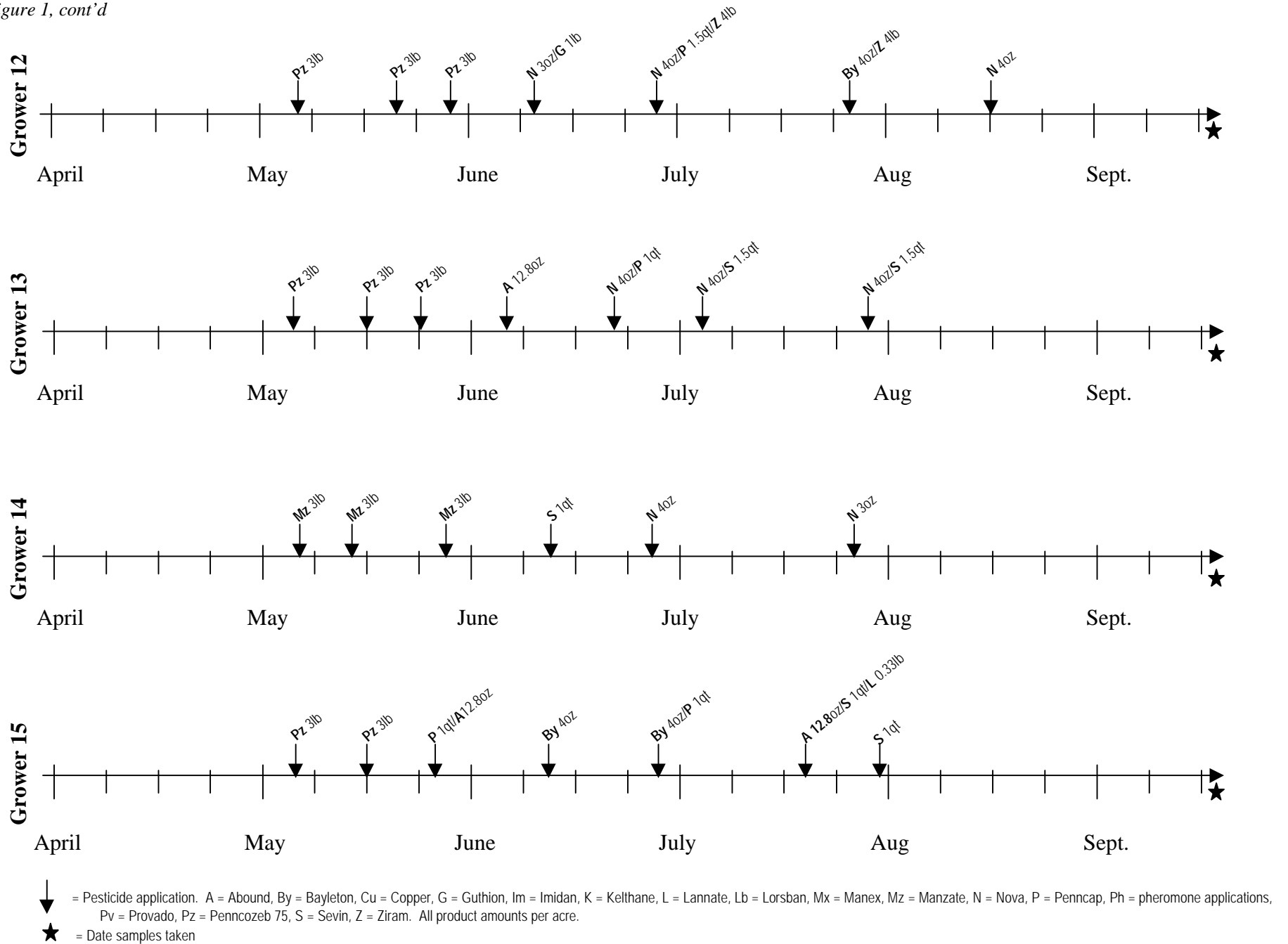


Figure 1, cont'd



↓ = Pesticide application. A = Abound, By = Bayleton, Cu = Copper, G = Guthion, Im = Imidan, K = Kelthane, L = Lannate, Lb = Lorsban, Mx = Manex, Mz = Manzate, N = Nova, P = Penncap, Ph = pheromone applications, Pv = Provado, Pz = Penncozeb 75, S = Sevin, Z = Ziram. All product amounts per acre.
 ★ = Date samples taken

Figure 1, cont'd



Appendix A—Materials and Methods

Harvest and handling

A. Research samples – grape berry moth pheromone plots:

Five Michigan grape growers (var. ‘Concord’) participated in a research trial comparing the effectiveness of pheromones with standard insecticide treatments for the control of the grape berry moth. The pesticides used and the timing of the applications are described in Figure 1.

Approximately 10 lbs. of grapes were collected by hand off the vines on 17 September 1998, just prior to harvest by the grower. Two samples were taken per grower: one pheromone plot sample, and one standard plot sample. The grapes were immediately stored in plastic bags and placed in the freezer (10°F) until residue analysis. All stems were removed from the grapes prior to residue analysis.

B. Grower samples – fresh:

Ten Michigan grape growers (var. ‘Concord’), representing a broad range of pesticide use strategies, participated in this study. The pesticides used by these growers and the timing of the applications are shown in Figure 1. Approximately 10 lbs. of grapes were collected by hand off the vines on 17 September 1998, just prior to harvest by the grower. The grapes were immediately stored in plastic bags and placed in the freezer (10°F) until residue analysis.

Pesticide Residue Analysis

- I. The Laboratory Division of the Michigan Department of Agriculture performed the residue analysis. All samples were delivered to the laboratory in October 1998. The samples arrived in the laboratory frozen. Samples were stored in a freezer, then thawed prior to grinding and extraction. Preparation of the sample followed Section 102 of the Pesticide Analytical Manual (PAM) Vol. 1 (pp.102-1—102-3). None of the samples were washed prior to analysis. The whole commodity was used after discarding leaves and stems.
- II. The extraction method used for most of the compounds was the “Luke II modified Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods.” This is a modification of the “Acetone Extraction Screening Method for Pesticide Residues in Non-Fatty, High Moisture Foods,” (Pesticide Analytical Manual, Vol. I, Sect. 302, U.S. Department of Health and Human Services, Food and Drug Administration). This is a multi-residue method for the analysis of organohalogen, organonitrogen, organophosphate, organosulfur, and carbamate pesticide residues in nonfatty, high moisture matrices, and returns both quantitative and qualitative results. Analysis of all the compounds except the carbamates was by Gas Chromatography/Mass Spectroscopy (GC/MS). Analysis of the carbamates was by Liquid Chromatography/Post-Column Derivatization/Fluorescence Detection, with carbaryl confirmation by MS.
- III. The extraction and analysis method used for Benomyl was from “HPLC Fluorometric Analysis of Benomyl and Thiabendazole in Various Agricultural Commodities” (Bulletin #3650, E. J. Wojtowicz).
- IV. Dithiocarbamates were analyzed using the Lowen and Pease method (G. Zweig [Ed.], 1964. Analytical methods for Pesticides, Plant Growth Regulators, and Food Additives, p. 65. *In* Fungicides, Nematocides and Soil Fumigants, Rodenticides, and Food and Feed Additives, Vol. III, Academic Press).
- V. Limits of Detection were originally set by analyzing a set of spikes at or near the believed limit of detection. The standard deviation was determined and multiplied by the student’s T, at the 99% confidence level, to calculate the limit of detection. If the calculated limit of detection appeared excessively low or high, a set of spikes was analyzed at a level thought to be more realistic, based on the signal to noise ratio. If all of these new spikes were detected and confirmed, then this became the new limit of detection. These were determined in one commodity and then assumed to be the same in other commodities unless spike recovery data indicated otherwise.
- VI. Tolerances were from Duggan (1998, Pesticide Chemical News Guide, CRC Press LLC).

Appendix B—All pesticides included in the residue analysis of all grape samples.

Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)	Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)
3-Hydroxycarbofuran	M	0.002	0.4	Hexazinone	H	0.15	none
Acephate	I	0.63	none	Imazilil	F	2	none
Alachlor	H	0.019	none	Iprodione	F	0.065	60.0
Aldicarb	I	0.001	none	Lindane	I	0.063	1
Aldicarb Sulfone	M	0.002	none	Linuron	H	0.078	none
Aldicarb Sulfoxide	M	0.002	none	Malathion	I	0.17	8
Anilazine	F	0.15	none	Methamidophos	I	0.30	none
Atrazine	H	0.025	none	Methidathion	I	0.055	none
Azinphos-Methyl	I	0.09	5.0	Methomyl	I	0.002	5
Benomyl	F	0.06	10.0	Methyl Parathion	I	0.058	1
Captan	F	0.075	50	Metolachlor	H	0.045	none
Carbaryl	I	0.002	10	Mevinphos	I	0.15	0.5
Carbofuran	I	0.001	0.4	Myclobutanil	F	0.14	1.0
Chlorothalonil	F	0.005	none	Omethoate	I	0.17	1
Chlorpropham	H	0.066	none	Oxamyl	I	0.002	none
Chlorpyrifos	I	0.038	0.5 regional	Oxyfluorfen	H	0.045	0.05
Cypermethrin	I	0.20	none	p,p'-DDE	M	0.013	0.05 revoked
DCPA	H	0.013	none	p,p'-DDT	I	0.013	0.05 revoked
Diazinon	I	0.016	0.5	p,p'-Dicofol	I	0.22	5
Dichloran	F	0.050	10	Pendimethalin	H	0.035	0.1 pending
Dichlorvos	I	0.033	none	Pentachlorobenzene	O	0.013	not found
Dieldrin	I	0.050	none	Pentachloronitrobenzene	F	0.030	none
Dimethoate	I	0.036	1	<i>cis</i> -Permethrin	I	0.028	none
Diphenylamine	F	0.014	none	<i>trans</i> -Permethrin	I	0.038	none
Disulfoton	I	0.10	0.75	Phosalone	I	0.045	10.0
Endosulfan I	I	0.050	2.0	Phosmet	I	0.044	10
Endosulfan II	I	0.060	2.0	Phosphamidon	I	0.28	none
Endosulfan Sulfate	M	0.075	2.0	Propargite	I	0.050	10
Ethion	I	0.011	2.0	Simazine	H	0.035	0.25
Ethoprop	I	0.035	0.02 temporary	Thiabendazole	I	2	10.0
Ethyl Parathion	I	0.055	1	Triadimefon	I	0.17	1.0
Fenamiphos	I	0.2	0.10	Trifluralin	H	0.013	0.5 negligible
Fenvalerate	I	0.070	4 pending	Vinclozolin	F	0.038	6.0 revoked
Hexachlorobenzene	F,I	0.023	not found				

^aF = Fungicide, H = Herbicide, I = Insecticide, M = Metabolite (break-down product), O = Other, *e.g.*, contaminant of the production process.

Peaches

Introduction

Peaches (*Prunus persica* L.) are woody perennials in the Rosaceae family and, along with plums, apricots, almonds, nectarines, and cherries, are referred to as “stone fruits” because of the hard central seed. Peach trees are typically grafted onto rootstocks. Peaches require light well-drained soil, as trees are susceptible to flooding in heavy or poorly drained soils. Good orchard sites should be selected with elevation and sloping topography to avoid damaging spring frosts; winter hardiness is also a concern in Michigan.

Peaches were grown on 5500 acres in Michigan, primarily in the southwest region of the state. Peach production rose significantly to 61 million pounds in 1997, an increase of more than 50% from the previous year. The total value of peach production in Michigan was \$16 million in 1997.

Major Pests

Oriental Fruit Moth (*Grapholita molesta*). This insect is a significant pest of peaches in the North Central region. First-generation adults appear in early May, with their larvae feeding on actively growing terminals of peach trees. Second-generation adults appear in mid-July and their larvae feed internally on the fruit, as well as the actively growing tips of branches. Third-generation adults appear in late August, and their larvae also feed in the fruit. Damage to terminal shoots stunt proper growth and tree structure, and larval infestation of fruit results in an unmarketable crop.

Peach Tree Borer (*Synanthedon exitiosa*). Stone fruits are attacked by these clearwing moths, the larvae causing damage by feeding in the inner bark or cambium layer of the tree trunk, which disrupts nutrient flow within the tree.

Lesser Peachtree Borer (*Synanthedon pictipes*). While very similar to the peach tree borer, the lesser peachtree borer emerges over a longer time during the summer (requiring additional pesticide applications), and the larvae can be found in the trunks, scaffold limbs, and branches. If not controlled, they may feed until the entire branch or limb is killed.

Plantbug (various species). The tarnished plant bug is an important pest of peaches, although numerous other plant bugs also attack this fruit. Injuries include blossom injury and fruit drop, cat-facing injury (puckered scars), scarring, water-soaking injury, and gummosis. Plant bugs cause blossom-and fruit-drop by piercing during feeding. Cat-facing injury from plant bugs results in fruit deformation.

Leaf Curl (*Taphrina deformans*). Once this fungus infects leaves in the spring, there is no effective treatment; therefore, fungicides must be applied preventatively. Infection occurs at bud burst. Leaves become thick, curled, and crinkled, turning orange or red; shoots and fruit can also be infected. When the fungus sporulates the leaves will become powdery, and eventually fall off the tree. Peach leaf curl weakens the tree by early defoliation, which may also cause fruit drop and reduce the size of the remaining fruit. Adequate control of leaf curl can be achieved by using a single application of an appropriate fungicide in the autumn or prior to bud burst in the spring.

Brown Rot and Blossom Blight (*Monilinia fructicola*). This fungus reduces yield by rotting the fruit either on the tree or after harvest. Favorable wetting conditions combined with warmer temperatures (77°F) can result in infection of the blossoms within a few hours. Infected blossoms wilt, turn brown, and remain on the tree during the summer. The damage on fruits begins with small, circular, light brown spots growing on the surface, and in wet, humid, warm

weather, the fruit maybe destroyed within a few days. Fruit decay is more common on mature fruit than immature fruit. Rotted fruit either falls to the ground or persists as mummies. The fungus then moves from the infected fruit to the branches, where new leaf and stem growth withers and dies. Sanitation combined with a protective fungicide program helps control this disease.

Pesticides Used

1. Azinphos-methyl (Guthion)

Non-systemic, broad-spectrum organophosphate insecticide used to control plum curculio and oriental fruit moth.

Oral LD₅₀ (rats) = 5 mg per kg body weight

Dermal LD₅₀ (rabbits) = 220 mg per kg body weight

Persistence in soil dependent upon soil type, ranging from 30-days to 1-year breakdown time.

On vegetation, the approximate residual period is 1-3 weeks

21 day PHI

2. Carbaryl (Sevin)

Broad-spectrum, systemic, cholinesterase inhibitor, widest use of any insecticide. Used to control oriental fruit moth, rose chafer, lecanium scale, earwigs and Japanese beetle.

Oral LD₅₀ (rats) = 307 mg per kg body weight

Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Insecticidal properties on crop for 3-10 days. Half life in aerobic soil 7 days, anaerobic 28 days.

3 day PHI

3. Chlorpyrifos (Lorsban)

This is a heterocyclic organophosphate contact insecticide used to control peach tree borers (lesser and greater). Foliar formulation not registered for peach, with only trunk sprays allowable.

Oral LD₅₀ (rats) = 135 mg per kg body weight

Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Moderately persistent but relatively immobile. The half-life ranges from 11-141 days depending on soil type, soil pH, and aerobic conditions.

14 day PHI

4. Esfenvalerate (Asana)

Broad-spectrum pyrethroid, used to control plum curculio, oriental fruit moth, green fruitworm, and plant bugs.

Oral LD₅₀ (rats) = 75 mg per kg body weight

Dermal LD₅₀ (rabbits) > 2000 mg per kg body weight

Half-life in soil is from 15 days to 3 months.

14 day PHI

5. Methomyl (Lannate)

A systemic carbamate insecticide used to control oriental fruit moth, plant bugs, rose chafer, and green peach aphids.

Oral LD₅₀ (rats) = 17 mg per kg body weight

Dermal LD₅₀ (rabbits) = 1000 mg per kg body weight

The dissipation half-life is 3-6 weeks in soil. It is highly soluble in water, increasing the chances for ground water contamination.

4 day PHI

6. Permethrin (Ambush, Pounce)

Broad-spectrum synthetic pyrethroid insecticide. Used to control climbing cutworms, tarnished plant bugs, green fruit worms, plum curculio and oriental fruit moth.

Oral LD₅₀ (rats) > 4000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 4000 mg per kg body weight

Breaks down quickly in the environment and on vegetation, allowing for short pre-harvest intervals

7 day PHI

7. Phosmet (Imidan)

Non-systemic, organophosphate insecticide. Used to control plum curculio and oriental fruit moth.

Oral LD₅₀ (rats) = 147 mg per kg body weight

Dermal LD₅₀ (rabbits) = 3160 mg per kg body weight

Half-life in sandy loam soil 3-19 days, with increasing rates of breakdown in higher pH

14 day PHI

8. Benomyl (Benlate)

A systemic fungicide with a wide spectrum of activity; in peaches, used for brown rot and powdery mildew.

Oral LD₅₀ (rats) > 10,000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight

Benomyl is strongly bound to soil. The half-life is 6-12 months.

3 day PHI

9. Captan

Non-systemic sulfenimide fungicide, used to control brown rot, powdery mildew, and peach scab.

Oral LD₅₀ (rats) = 9000 mg per kg body weight

No dermal irritation

Half-life in soil 1-10 days, with activity on potato foliage for 23 days.

0 days PHI.

10. Chlorothalonil (Bravo)

Substituted aromatic, broad-spectrum foliage-protectant fungicide, used to control peach leaf curl, brown rot, and powdery mildew.

Oral LD₅₀ (rats) > 10,000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight

“Fairly persistent” on crop surfaces. Half-life in aerobic soils 1-3 months

Do not apply between shuck split and harvest.

11. Copper (Kocide, Champ, COCS)

Used as copper sulfate with lime and as copper hydroxide; protectant fungicide against leaf curl and bacterial spot.

Oral LD₅₀ (rats) = 300 (sulfate) or 1000 (hydroxide) mg per kg body weight

Dermal irritant

No PHI restrictions if applied per label instructions

12. Myclobutanil (Nova)

A systemic fungicide with curative and protective qualities. Used to control brown rot and powdery mildew.

Oral LD₅₀ (rats) = 1600 mg per kg body weight

Dermal LD₅₀ (rabbits) > 5000 mg per kg body weight

7 day PHI

13. **Sulfur** (Sulfur, Thiolux)

One of the oldest effective fungicides known, both systemic and non-contact, used to control peach scab, powdery mildew, and brown rot.

Oral LD₅₀ (rats) > 5000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 5000 mg per kg body weight

PHI: Exempt

Materials and Methods—see Appendix A

Pesticides used listed in Table 1.

Results and Discussion

A total of 58 peach samples, all from commercial orchards, were examined for residues. Partially processed samples were tested, including washed, brushed, peeled, or halved peaches, and one fully processed (bottled) sample. All samples were tested for a total of 68 pesticides and metabolites (Appendix B). Of these, nine pesticides were detected from these samples.

The peach growers in this study applied five different organophosphate insecticides (Tables 1 and 2). Azinphos-methyl and phosmet were used by the most growers (ten and nine, respectively), and in both cases at rates less than the potential maximum use (Table 2). In addition, the mean pre-harvest intervals observed were three times longer than the labeled PHI (Table 2). Azinphos-methyl was not detected on any sample (Table 2), and phosmet was detected on 12 samples (9 raw, 3 washed or brushed), representing 21% of the total. The highest phosmet residue was 2 ppm, which is five-fold less than current tolerance. Washing or brushing the fruit prior to analysis decreased the mean residue of phosmet, from 0.29 to 0.12 ppm (Table 3). The other organophosphates applied were chlorpyrifos (one grower), methyl parathion (four growers), and methidathion (one grower), with no residues detected for any of these products.

Carbaryl and methomyl were used by these peach growers, with five samples having detectable residues of each pesticide (Table 2). The amount of residue was never more than 6% of the current tolerance. For carbaryl, the mean residue decreased from the off-tree samples to the washed or brushed samples (Table 3), but there was little change with processing in those samples containing methomyl.

Of the pyrethroids, esfenvalerate was used by the most growers (21). The total amount of product used by each of these growers ranged from 1.6- to 5-fold less than the maximum potential use based on label restrictions, and observed preharvest intervals exceeding the labeled PHI by 1 to 99 days (Table 2). Only two samples had detectable esfenvalerate residues, 20-fold less than the current tolerance (Table 2). Seven growers used permethrin, with four samples having detectable residue (Table 2). The highest amount of residue found was 50 times less than current tolerance. Washing the samples did not decrease the amount of permethrin detected (Table 3).

Every peach grower in this study applied fungicides. Various formulations of two inorganic fungicides, sulfur and copper, were applied by every grower, but were not included in the residue analysis. Of the synthetic products used, propiconazole and tebuconazole were the most commonly applied. Myclobutanil was used by five growers, yet only one sample had detectable residues of this product, at an amount five-fold less than current tolerance (Table 2). Three

growers used benomyl, with five samples having detectable residues (Table 2); the residue amount was 15-fold less than current tolerance. The B2-carcinogenic fungicides captan and chlorothalonil were used by eight and three growers, respectively (Table 2). Seven samples were positive for captan, at 50-fold less than current tolerance. Growers who used captan applied it at rates less than half of the potential use (based on labeled maximum use restrictions), and from 10 to 103 days before harvest (labeled PHI was one day). Despite a long pre-harvest interval for chlorothalonil of 118 to 135 days, two samples had detectable chlorothalonil residue, five-fold less than current tolerance (Table 2).

There were no pesticide residues found in any sample that had been peeled or canned as halves, even if there were residues found in the off-tree sample. The grower who provided the single sample of bottled peaches applied permethrin, endosulfan, and captan to that orchard, yet this sample did not contain any of those pesticides, nor any of the other pesticides listed in Appendix B.

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Table 1. Summary of Insecticides and Fungicides Registered for Use on Peaches.

Common Name	Trade name	Type ¹	Common Name	Trade name	Type ¹
<i>Used during 1998 ²</i>			<i>Labeled but not used 1998 ²</i>		
azinphos-methyl	Guthion	OP	diazinon	Spectracide	OP
carbaryl	Sevin	Carb	dormetanate hydrochloride	Carzol	O
chlorpyrifos	Lorsban	OP	vinclozolin	Ronilan	O
endosulfan	Thiodan	OC			
esfenvalerate	Asana	O			
methidathion	Supracide	OP			
methomyl	Lannate	Carb			
methyl parathion	Penncap-M	OP			
permethrin	Pounce/Ambush	O			
phosmet	Imidan	OP			
benomyl	Benlate	O			
captan	Captan	O			
dithiocarbamate	Ferbam	Carb			
chlorothalonil	Bravo	B2			
clofentezine	Apollo	O			
copper sulfate, copper hydroxide	Bordeaux mixture, Kocide, Champ	O			
EBDC	Various	B2			
fenbuconazole	Indar	O			
iprodione	Rovral	O			
myclobutanil	Nova	O			
propiconazole	Orbit	O			
sulfur	Sulfur, Thiolux	O			
tebuconazole	Elite	O			
triadimefon	Bayleton	O			
ziram	Ziram	O			

¹ B2 = B2 carcinogen; Carb = carbamate; OP = organophosphate; OC = organochlorine; O = other category.

² Refers to pesticides used by Michigan growers in this study.

Table 2. Potential and actual product use in peaches, 1998, with pre-harvest intervals and residue found.

Product	<i>n</i> ^a	Maximum Rate ^b	Actual Total Use (rate X #app)		PHI ^c (days)	Actual PHI (days)		Tolerance (ppm)	Residue Results		
			Mean	Range		Mean	Range		No. (%) Positive Samples	Mean (ppm)	Range (ppm)
azinphos-methyl	10	9 lb	2.8 lb	1-7.5	21	75	42-118	2	0	--	--
carbaryl	1	17.5	4 lb	--	3	10	--	10	5 (8.6)	0.11	0.03-0.2
chlorpyrifos	1	1.5 qt	1.5 qt	--	14	74	--	0.05	0	--	--
esfenvalerate	21	72.5 oz	15.3 oz	4-45	14	77	15-113	10	2 (3.4)	0.45	0.4-0.5
methomyl	6	5.4 lb	1.4 lb	0.45-3.6	4	63	8-100	5	5 (8.6)	0.10	BQL ^d -0.3
methyl parathion	4	36 pt	6.6 pt	4.5-8	28	61	57-65	1	0	--	--
permethrin	7	120 oz	11.5 oz	4-17.5	5	87	14-224	5	4 (6.9)	0.08	0.05-0.1
phosmet	9	17 lb	4.4 lb	1.5-10	14	43	17-80	10	12 (20.6)	0.25	0.05-2.0
benomyl	3	-- ^e	7.2 lb	0.5-18	3	43	10-68	15	5 (8.6)	0.38	0.09-1.0
captan	8	64 lb	10.25 lb	1.5-31	1	60	10-103	50	7 (12.1)	0.33	0.1-0.9
chlorothalonil	3	-- ^e	6.3 pt	5-8	Shuck split	123	118-135	0.5	2 (3.4)	0.06	0.01-0.1
myclobutanil	5	44 oz	10.7 oz	3-20	1	65	34-130	2	1 (1.7)	0.4	--

^aNumber of growers out of 32 who reported application of this product in 1998.

^bBased on 1998 product label.

^cLabeled pre-harvest interval in days.

^dBQL, below quantifiable limit.

^eNo maximum use on 1998 label.

Table 3. Residue comparison between off-tree and processed peach samples, including only those samples that had residues in the processed product.

Product Source (# in each type)	Tolerance (ppm)	Residue Results		
		No. (%) Positive Samples	Mean (ppm)	Range (ppm)
carbaryl	10	5 (8.6)	0.11	0.03-0.2
Off-tree		1	0.2	--
Washed (2) or Brushed (1)		4	0.09	0.03-0.2
methomyl	5	5 (8.6)	0.10	BQL^d-0.3
Off-tree		2	0.05	BQL-0.1
Washed		3	0.13	0.03-0.3
permethrin	5	4 (6.9)	0.08	0.05-0.1
Off-tree		2	0.08	0.06-0.1
Washed		2	0.08	0.05-0.1
phosmet	10	12 (20.6)	0.25	0.05-2.0
Off-tree		9	0.29	0.05-2.0
Washed (2) or Brushed (1)		3	0.12	0.05-0.2
benomyl	15	5 (8.6)	0.38	0.09-1.0
Off-tree		1	1.0	--
Washed (3) or Brushed (1)		4	0.22	0.09-0.5
captan	50	7 (12.1)	0.33	0.1-0.9
Off-tree		3	0.43	0.2-0.9
Washed (3) or Brushed (1)		4	0.25	0.1-0.5

Appendix A – Materials and Methods

Harvest and handling

A. Grower samples – raw vs. blanch peeled:

Thirteen Michigan peach growers participated in this study. These growers represented a broad range of pesticide usage; the pesticides used by these growers in 1998 are listed in Table 1.

Approximately 20 lbs. of peaches were sampled from each grower immediately after harvest in late August 1998. Half of the peaches from each grower were immediately stored in plastic bags in the freezer (10°F) until residue analysis. For Growers #1, 2, and 7, the other half of the peaches in the sample were washed in warm soapy well water, rinsed two times in cold well water, and then stored in the freezer as described above. For the other ten growers, the other half of the peaches in the sample were dropped in boiling water for two minutes, dropped in ice water, and then entirely peeled. The water was changed between samples. The blanched and peeled peaches from these growers were stored in the freezer (10°F).

B. Grower samples – raw vs. washed:

Ten Michigan peach growers, representing a broad range of pesticide use strategies, participated in this study. The varieties of these fresh-market peaches included ‘Adkin’, ‘Cresthaven’, ‘Flamin Fury’, ‘Harcrest’, ‘Newhaven’, and ‘Redkist’. Pesticides used by these growers in 1998 are listed in Table 1.

Approximately 20 lbs. of peaches were sampled from each grower immediately after harvest in late August, before any washing or brushing treatments. For Growers #6, 7, 8, and 10, the peaches were stored in plastic bags in the freezer (10°F) until residue analysis. For Growers #1, 2, 3, 4, 5, and 9, half of the peaches from each grower were frozen immediately. The other half of the peaches from these growers were subjected to cold water wash treatment(s) during hydrocooling and/or grading before they were frozen for analysis.

C. Grower samples – raw vs. processed:

Eight Michigan peach growers (variety ‘Baby Gold 5’, for processing) participated in this study. Pesticides used by these growers in 1998 are listed in Table 1.

Approximately 10 lbs. of peaches were sampled from each grower in early September. Five lbs. of raw, unwashed peaches per grower were sampled before the canning process, and 5 lbs. of peeled peach halves per grower were sampled after the canning process. These samples were stored in plastic bags and frozen until residue analysis.

D. Grower samples – processed:

One Michigan peach grower (variety Baby Gold 5) submitted 5 lbs. of bottled peaches in August 1998. The canned sample was held at room temperature until residue analysis in December 1998.

Pesticide Residue Analysis

The Laboratory Division of the Michigan Department of Agriculture performed the residue analysis.

- I. The samples arrived in the laboratory frozen, September 1998. They were stored in a freezer, then thawed prior to grinding and extraction. Preparation of the sample followed Section 102 of the Pesticide Analytical Manual (1997, Vol. 1, 3rd edition, U.S. Dept. of Health and Human Services, Public Health Service, Food and Drug Administration, pp.102-1—102-3). None of the samples were washed prior to analysis. The whole portion of the submitted samples was used after discarding stems and pits.
- II. The extraction method used for most of the compounds was the “Luke II modified Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods.” This is a modification of the “Acetone Extraction Screening Method for Pesticide Residues in Non-Fatty, High Moisture Foods,” (Pesticide Analytical Manual, 1997, Vol. I, Sect. 302, U.S. Dept. of Health and Human Services, Food and Drug Administration). This is a multi-residue method for the analysis of organohalogen, organonitrogen, organophosphate, organosulfur, and carbamate pesticide residues in nonfatty, high moisture matrices, and returns both quantitative and qualitative results. Analysis of all the compounds except the carbamates was by Gas Chromatography/Mass Spectroscopy (GC/MS). Analysis of the carbamates was by Liquid Chromatography/Post-Column Derivatization/Fluorescence Detection, with carbaryl confirmation by MS.
- III. The extraction and analysis method used for Benomyl was from “HPLC Fluorometric Analysis of Benomyl and Thiabendazole in Various Agricultural Commodities” (Bulletin #3650, E. J. Wojtowicz)
- IV. Dithiocarbamates were analyzed using the Lowen and Pease method (G. Zweig [Ed.], 1964. Analytical methods for Pesticides, Plant Growth Regulators, and Food Additives, p. 65. *In Fungicides, Nematocides and Soil Fumigants, Rodenticides, and Food and Feed Additives*, Vol. III, Academic Press).

- V. Limits of Detection were originally set by analyzing a set of spikes at or near the believed limit of detection. The standard deviation was determined and multiplied by the student's T, at the 99% confidence level, to calculate the limit of detection. If the calculated limit of detection appeared excessively low or high, a set of spikes was analyzed at a level thought to be more realistic, based on the signal to noise ratio. If all of these new spikes were detected and confirmed, then this became the new limit of detection. These were determined in one commodity and then assumed to be the same in other commodities unless spike recovery data indicated otherwise.
- VI. Tolerances were from Duggan (1998, Pesticide Chemical News Guide, CRC Press LLC).

Appendix B—All pesticides included in the residue analysis of all peach samples

Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)	Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)
3-Hydroxycarbofuran	M	0.002	none	Imazilil	F	2	none
Acephate	I	0.63	none	Iprodione	F	0.065	20.0
Alachlor	H	0.019	none	Lindane	I	0.063	1
Aldicarb	I	0.001	none	Linuron	H	0.078	none
Aldicarb Sulfone	M	0.002	none	Malathion	I	0.17	8
Aldicarb Sulfoxide	M	0.002	none	Methamidophos	I	0.30	none
Anilazine	F	0.15	none	Methidathion	I	0.055	0.05 negligible
Atrazine	H	0.025	none	Methomyl	I	0.002	5
Azinphos-Methyl	I	0.09	2	Methyl Parathion	I	0.058	1
Benomyl	F	0.05	15.0	Metolachlor	H	0.045	none
Captan	F	0.075	50	Mevinphos	I	0.15	1.0
Carbaryl	I	0.002	10	Myclobutanil	F	0.14	2.0
Carbofuran	I	0.001	none	Omethoate	I	0.17	none
Chlorothalonil	F	0.005	0.5	Oxamyl	I	0.002	none
Chlorpropham	H	0.066	none	Oxyfluorfen	H	0.045	0.05
Chlorpyrifos	I	0.038	0.05	p,p'-DDE	M	0.013	0.5 revoked
Cypermethrin	I	0.20	none	p,p'-DDT	I	0.013	0.5 revoked
DCPA	H	0.013	none	p,p'-Dicofol	I	0.22	10
Diazinon	I	0.016	0.7	Pendimethalin	H	0.035	none
Dichloran	F	0.050	20	Pentachlorobenzene	O	0.013	not found
Dichlorvos	I	0.033	none	Pentachloronitrobenzene	O	0.030	none
Dieldrin	I	0.050	none	<i>cis</i> -Permethrin	I	0.028	5.0
Diphenylamine	F	0.014	none	<i>trans</i> -Permethrin	I	0.038	5.0
Disulfoton	I	0.10	none	Phorate	I	0.042	none
Endosulfan I	I	0.050	2.0	Phosalone	I	0.045	15.0
Endosulfan II	I	0.060	2.0	Phosmet	I	0.044	10
Endosulfan Sulfate	M	0.075	2.0	Phosphamidon	I	0.28	none
Ethion	I	0.011	1.0	Propargite	I	0.050	7
Ethoprop	I	0.035	none	Simazine	H	0.035	0.25
Ethyl Parathion	I	0.055	1	Terbufos	I	0.025	none
Fenamiphos	I	0.2	0.25	Thiabendazole	I	2	none
Fenvalerate	H	0.070	10.0	Triadimefon	I	0.17	4.0
Hexachlorobenzene	F,I	0.023	not found	Trifluralin	H	0.013	0.05 negligible
Hexazinone	H	0.15	none	Vinclozolin	F	0.038	25.0

^aF = Fungicide, H = Herbicide, I = Insecticide, M = Metabolite (break-down product), O = Other, *e.g.*, contaminant of the production process.

Potatoes

Introduction

The potato, *Solanum tuberosum*, is an important food crop throughout the world, ranking fourth in world production after wheat, corn, and rice. Potato plants develop from sprouting eyes on seed pieces (tubers). As plants grow during the vegetative stage, leaves and branches develop aboveground on stems. Another kind of stem - called stolons - develops below ground. Tuber initiation begins in early to mid-season, around the time of flowering. During this brief stage, which last 10 to 14 days, tubers form at the tips of the stolons. During the rest of the season, tubers undergo bulking as carbohydrates, water, and other nutrients fill the tuber cells and cause them to increase in size. Finally, late in the season, the potato plants mature. Above ground, vines turn yellow and senesce; below ground, tubers reach maximum growth and set a thick skin. Potatoes are vegetatively propagated (ie. from tubers), which tends to exacerbate key disease and insect problems.

In 1998, Michigan growers harvested 47,500 acres of potato. Average yields in Michigan can range between 250 and 300 hundredweight (= 100 pounds) per acre. While Michigan ranks ninth in the nation for total potato production, it is one of the leading states in production of potatoes for chipping. Much of the Michigan potato harvest is targeted for processing, with 65% going for chipping and 3% for freezing. Fresh market potatoes account for another 27% of the total harvest. The remaining production, about 5% of the acreage, is managed as seed potato. Seed potato usually receives heavy inputs of pesticide, but generally does not enter the food chain. The total value of Michigan potatoes in 1998 was \$94 million.

Major Pests

Potato Late Blight (*Phytophthora infestans*). Late blight - the cause of the Irish potato famine - is the most important potato pathogen worldwide, and has become increasingly devastating in the United States. Unchecked, late blight will cause 100% loss of the potato crop. The late blight fungus overwinters on seed potatoes, tubers missed during harvest, or culls dumped near farms. In the spring, the fungus infects the sprouting tubers, producing spores. The infection then spreads via air or water to other tubers and fields, especially when conditions are cool and wet. Infected leaves have distinct necrotic lesions that may increase under favorable conditions and kill the plant. Infected tubers also develop lesions that grow slowly in cold storage. However, secondary organisms can infect the lesions and lead to partial or complete rotting of the tubers. Late blight control has recently become more difficult in the United States with the advent of resistance to some fungicides, plus the discovery of new genetic strains of the fungus, previously present only in south and central America. The new strains allow the late blight fungus to form hardy overwintering spores that can remain free in the soil for months or years.

Insect pests (various spp.). A number of important insects are major limiting factors to potato production. These include Colorado potato beetle and potato leafhopper. However, insect pests - and thus insecticides - were not the focus of the potato residue study, and will not be discussed in detail in this report.

Pesticides Used

1. Chlorothalonil (Bravo, Terranil)
Substituted aromatic, broad-spectrum foliage-protectant fungicide, used on many fruit, vegetable, turf, and ornamental crops.
Oral LD₅₀ (rats) > 10,000 mg per kg body weight
Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight
“Fairly persistent” on crop surfaces. Half-life in aerobic soils 1-3 months.
7 day pre-harvest interval (PHI)
2. Mancozeb (Penncozeb, Manzate, others)
Wide-spectrum EBDC fungicide with uses in fruit, field, and vegetable crops.
Oral LD₅₀ > 8000 mg per kg body weight
No dermal toxicity
Non- to moderately persistent (up to 18 months) in the environment.
3 day PHI
3. Triphenyltin hydroxide (Super Tin)
Tin-based organic fungicide.
Oral LD₅₀ = 160 mg per kg body weight
Dermal LD₅₀ = 500 mg per kg body weight
Non- to moderately persistent. Severe skin irritant.
21 day PHI
4. Propamocarb hydrochloride (Tattoo)
Used in 1998 in Michigan under a Section 18 label to control potato late blight. Used in combination with chlorothalonil as “Tattoo C”.
Oral LD₅₀ (rats) = 2000 mg per kg body weight
Dermal LD₅₀ (rabbits) > 3900 mg per kg body weight
14 day PHI

Materials and Methods – See Appendix A

Results and Discussion

A total of 38 potato samples, all from Michigan State University research plots, were examined for pesticide residues. Only a limited number of pesticides were used in the university research plots, compared to the number of pesticides available to growers in Michigan (Table 1). All samples were tested for a total of 72 different pesticides and metabolites (Appendix B). No pesticides were detected in any sample (Tables 2 and 3).

Although insecticides were not the target of the potato residue analysis, four different insecticides were applied to all plots (including the “check” plots not treated with fungicides). Actual use rates were well below label maximum rates, and actual pre-harvest intervals were many times greater than label PHIs (Table 2). Residues of carbaryl, endosulfan, and permethrin were not detected in any potato sample. The Department of Agriculture Laboratory was unable to test for the fourth insecticide, imidacloprid, so no conclusions can be drawn about residues resulting from the use of Admire at planting.

Residue analysis was performed on samples from plots representing a wide range of fungicide use patterns. Different types of fungicides were compared individually and in combination, including chlorothalonil (Bravo, Terranil), EBDCs (Penncozeb, Manzate), metalaxyl

(Ridomil), organotin (Super Tin), and propamocarb hydrochloride (Tattoo) (Table 3). Application rates varied both between plots (for example, Bravo was applied to different plots at rates from 0.5 to 1.5 pints per acre) and within plots (for example, Terranil was applied to the same plots in increasing or decreasing amounts throughout the season). Also, spray intervals varied for some products between five and seven days. Since prevention of late blight requires frequent applications of fungicide, the actual amounts used of many of the products in the research plots approached or even exceeded the label maximum (potential) use rate (Table 3). However, despite the wide range in fungicide types and use practices, from moderate to heavy usage, no residue of chlorothalonil, EBDCs, metalaxyl, or propamocarb hydrochloride was found in any of the 38 samples. The Department of Agriculture Laboratory did not test for triphenyltin hydroxide, the active ingredient in Super Tin, so no conclusions can be drawn about the use of that compound.

It is not necessarily surprising that fungicide residues were not detected in this study. First, potatoes are underground, and are thus not directly sprayed with pesticide. Second, actual pre-harvest intervals in the research plots were from two to twenty-two times greater than label PHIs, depending on the fungicide. Potato vines senesce in the fall, and remaining foliage is usually killed with a desiccant or defoliant at the end of the season. Since tubers are underground and protected from frost, potatoes may not be harvested for weeks or months after the last fungicide application to green foliage. This extra time obviously plays a role in reducing any residue potentially found on the tubers.

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Table 1. Summary of Insecticides and Fungicides Registered for Use on Potatoes.

Active Ingredient	Trade Name	Type ¹	Detection Limit (ppm)	Tolerance (ppm)	Detected
<i>Used during 1998</i> ²					
carbaryl	Sevin	Carb	0.001	0.2	No
chlorothalonil	Bravo, Terranil	B2	0.005	0.1	No
endosulfan	Thiodan	Other	0.05	0.2	No
imidacloprid	Admire	Other	-- ³	-- ³	-- ³
mancozeb	Manzate Penncozeb	B2	1.0	1.0	No
metalaxyl	Ridomil	Other	0.084	0.5	No
permethrin	Pounce	Other	0.028	0.05	No
propamocarb hydrochloride	Tattoo	Other	-- ⁴	0.5	No
triphenyltin hydroxide	Super Tin	Other	-- ³	-- ³	-- ³
<i>Others labeled, but not used in 1998</i> ²					
azinthosmethyl	Guthion	OP	0.009	0.3	No
carbofuran	Furadan	Carb	0.001	2.0	No
diazinon	Diazinon	OP	0.016	0.1	No
disulfoton	Di-Syston	OP	0.10	0.75	No
esfenvalerate	Asana	Other	0.07	0.02	No
imidacloprid	Provado	Other	-- ³	-- ³	No
iprodione	Rovral	Other	0.065	0.5	No
methomyl	Lannate	Carb	0.002	0.2	No
methyl parathion	Penncap	OP	0.058	0.1	No
phosmet	Imidan	OP	0.044	0.1	No

¹ B2 = B2 carcinogen; Carb = carbamate; OP = organophosphate; Other = other category.

² Used in this 1998 experiment.

³ Was not tested for by the Michigan Department of Agriculture.

⁴ Unable to analyze limit of detection.

Table 2. Insecticides applied in all Michigan State University potato late blight research plots in 1998.

Insecticides	No. of Samples	Application Rate/acre	No. of Applications	Total actual use (rate x # appl.)	<i>Potential (label) use</i>	PHI (days)		No. Positive Samples
						<i>Label</i>	Actual	
Admire 2F	38	20 oz	1	20 oz	20 oz	-- ^a	101	-- ^b
Pounce 3.2EC	38	8 oz	1	8 oz	96 oz	7	74	0
Sevin 80S	38	1.25 lb	2	2.5 lb	7.5 lb	7	74	0
Thiodan 3EC	38	2.33 pt	2	4.66 pt	8.0 pt	1	45	0

^a Admire applied at planting; no labeled pre-harvest interval.

^b Michigan Department of Agriculture Lab was unable to test for Admire.

Table 3. Fungicide treatment regimes, potential versus actual use rates and pre-harvest intervals, and resulting residue in Michigan State University potato late blight research plots, Bath, Michigan, 1998.

Single fungicide, single rate:

Fungicides	No. of Samples	Application rate/acre	No. of Applications	Application Scheme	Total Actual Use (rate x # appl.)	<i>Potential (label) Use</i>	PHI (days)		No. Positive Samples
							<i>Label</i>	Actual	
CHECK	2	-	0	--	0 lb	--	--	--	0
Bravo WS	2	0.5 pt	9	weekly	4.5 pt	16.0 pt	7	45	0
Bravo WS	2	1.0 pt	9	weekly	9.0 pt	16.0 pt	7	45	0
Bravo WS	2	1.5 pt	9	weekly	13.5 pt	16.0 pt	7	45	0
Bravo ZN	2	1.5 pt	14	every 5 days	21.0 pt	23.0 pt	7	38	0
Penncozeb	2	2.0 lb	9	weekly	18.0 lb	15.0 lb	3	45	0
Tattoo C	2	1.28 pt	9	weekly	11.5 pt	11.5 pt	14	45	0
Tattoo C	2	1.72 pt	9	weekly	15.5 pt	11.5 pt	14	45	0
Terranil ZN	2	1.5 pt	14	every 5 days	21.0 pt	21.0 pt	7	38	0

Single fungicide, variable rate:

Penncozeb	2	1.0 lb	1	week 1	15.8 lb	15.0 lb	3	45	0
		1.7 lb	4	weeks 2 - 5					
		2.0 lb	4	weeks 6 - 9					
Terranil ZN	2	1.0 pt	2	weeks 1, 2	14.9 pt	21.0 pt	7	45	0
		1.5 pt	3	weeks 3 - 5					
		2.1 pt	4	weeks 6 - 9					
Terranil ZN	2	2.1 pt	2	weeks 1, 2	12.7 pt	21.0 pt	7	45	0
		1.5 pt	3	weeks 3 - 5					
		1.0 pt	4	weeks 6 - 9					

Table 3, continued:

Multiple fungicides:

Fungicides	No. of Samples	Application rate/acre	No. of Apps.	Application Scheme	Total Actual Use (rate x # appl.)	Potential (label)Use	PHI (days)		No. Positive Samples
							Label	Actual	
Bravo WS Bravo + Ridomil	2	1.5 pt 1.5 / 0.2 pt	7 2	weeks 1, 3, 5 - 9 weeks 2, 4	B = 13.5 pt R = 0.4 pt	<i>B = 16 pt</i> <i>R = --^a</i>	<i>B = 7</i> <i>R = 3</i>	B = 36 R = 67	0
Bravo WS Tattoo C	2	1.5 pt 2.3 pt	7 2	weeks 1, 2, 4, 6 - 9 weeks 3, 5	B = 10.5 pt T = 4.6 pt	<i>B = 16 pt</i> <i>T = 11.5 pt</i>	<i>B = 7</i> <i>T = 14</i>	B = 36 T = 67	0
Bravo WS Tattoo C	2	1.5 lb 2.3 lb	6 3	weeks 1,2,4,6, 8, 9 weeks 3, 5, 7	B = 9.0 pt T = 6.9 pt	<i>B = 16 pt</i> <i>T = 11.5 pt</i>	<i>B = 7</i> <i>T = 14</i>	B = 45 T = 59	0
Manzate + Supertin	2	2.0 + 0.125 lb	9	weekly	M = 18.0 lb S = 1.12 lb	<i>M = --^b</i> <i>S = 0.9 lb</i>	<i>M = 3</i> <i>S = 21</i>	42	0
Manzate WP Manzate + Supertin Manzate + Supertin	2	2.0 lb 2.0 + 0.125 lb 2.0 + 0.23 lb	4 4 1	weeks 1 - 4 weeks 5 - 8 week 9	M = 18.0 lb S = 0.73 lb	<i>M = --^b</i> <i>S = 0.9 lb</i>	<i>M = 3</i> <i>S = 21</i>	42	0
Manzate WP Manzate WP Manzate + Supertin	2	1.0 lb 1.33 lb 2.0 + 0.23 lb	3 5 1	weeks 1 - 3 weeks 4 - 8 week 9	M = 11.6 lb S = 0.23 lb	<i>M = --^b</i> <i>S = 0.9 lb</i>	<i>M = 3</i> <i>S = 21</i>	42	0
Terranil WS Manzate DF	2	1.5 pt 2.0 lb	5 4	weeks 1,3,5,7, 9 weeks 2, 4, 6, 8	T = 7.5 pt M = 8.0 lb	<i>T = 21.5 pt</i> <i>M = 15 lb</i>	<i>T = 7</i> <i>M = 3</i>	T = 45 M = 52	0

^a Ridomil Gold EC formulation not labeled for use on potato; PHI taken from other Ridomil formulations.

^b Unable to find specific label maximum rate for Manzate WP formulation.

Appendix A—Materials and Methods

Potato samples were taken from Michigan State University fungicide research plots at the Muck Soils Experimental Station in Bath, MI. The primary purpose of these plots was to evaluate a wide range of fungicide use regimes for control of potato late blight. Approximately 70 different treatment regimes were tested in 1998; however, we concentrated on 19 of these treatments for residue analysis. A complete description of the treatments is given in Table 2. Plots were planted on 26 June and sprayed with fungicide every 5 or 7 days throughout the summer, depending on the assigned treatment. All plots were also treated with insecticides to control Colorado potato beetle and potato leafhopper. Harvest occurred in October.

Approximately 10 pounds of potato tubers were dug by hand from each plot in October 1998. Treatments sampled included checks (no fungicide), single fungicide treatments with a single season-long rate, single fungicide treatments with varying rates (increasing or decreasing rate during the season) and combination treatments of several different products. Three replicates of the 19 different treatments were harvested for a total of 57 samples. The samples were brought back to a university laboratory, and washed to remove excess dirt. Washing was done for two reasons. First, potatoes purchased by consumers in grocery stores are usually washed. Second, potatoes in this experiment were grown in muck soil, a very heavy, wet soil type that leaves a thick coating of soil on the tubers. Thus, a washing step was deemed necessary. Tubers from each of the 19 treatments were saved for processing (chipping; 19 samples total); the remainder of each sample was bagged and frozen. Samples were brought frozen to the Michigan Department of Agriculture laboratory in December. Due to constraints of time and money, the MDA laboratory ran only 2 replicates of samples (38 samples). The third replicate and chip samples were not tested after no fungicides were detected in the initial 38 samples.

Pesticide residue analysis

The Laboratory Division of the Michigan Department of Agriculture performed the residue analysis. All samples were delivered to the laboratory in December 1998.

- I. The samples arrived in the laboratory frozen. They were stored in the freezer, then thawed prior to grinding and extraction.
- II. Preparation of the sample followed Section 102 of the Pesticide Analytical Manual (1997, Vol. 1, 3rd edition, U.S. Dept. of Health and Human Services, Public Health Service, Food and Drug Administration, pp. 102-1 to 102-3). None of the samples were washed at the laboratory prior to analysis. The whole commodity was used in the analysis.
- III. The extraction method used for most of the compounds was the “Luke II modified Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods.” This is a modification of the “Acetone Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods” (Pesticide Analytical Manual, 1997, Vol. 1, Sect 302, U.S. Dept. of Health and Human Services, Food and Drug Administration). This is a multi-residue method for the analysis of organohalogen, organonitrogen, organophosphate, organosulfur, and carbamate pesticide residues in nonfatty, high moisture matrices, and returns both quantitative and qualitative results. Analysis of all compounds except the carbamates was by Gas Chromatography/Mass Spectroscopy (GC/MS). Analysis of the carbamates was by Liquid Chromatography/Post-Column Derivatization/Fluorescence Detection, with carbaryl confirmation by MS.
- IV. The extraction and analysis method for benomyl was from “HPLC Fluorometric Analysis of benomyl and Thiabendazole in various Agricultural Commodities” (Bulletin #3650, E.J. Wojtowicz).
- V. Dithiocarbamates were analyzed using the Lowen and Pease method (G. Zweig [Ed], 1964. Analytical methods for Pesticides, Plant Growth Regulators, and Food Additives, p. 65. *In* Fungicides, Nematicides and Soil Fumigants, Rodenticides, and Food and Feed Additives, Vol. III, Academic Press).
- VI. Limits of Detection were originally set by analyzing a set of spikes at or near the believed limit of detection. The standard deviation was determined and multiplied by the student’s T, at the 99% confidence level, to calculate the limit of detection. If the calculated limit of detection appeared excessively low or high, a set of spikes was analyzed at a level thought to be more realistic, based on the signal to noise ratio. If all of these new spikes were detected and confirmed, then this became the new limit of detection. These were determined in one commodity and then assumed to be the same in other commodities unless spike recovery data indicated otherwise.
- VII. Tolerances were from Duggan (1998, Pesticide Chemical News Guide, CRC Press LLC).

Appendix B—All pesticides included in the residue analysis of all potato samples

Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)	Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)
3-Hydroxycarbofuran	M	0.002	2	Iprodione	I	0.065	0.5
Acephate	I	0.63	none	Lindane	I	0.063	0.5 regional
Alachlor	H	0.019	none	Linuron	H	0.078	1.0
Aldicarb	I	0.001	1	Malathion	I	-- ^b	none
Aldicarb Sulfone	M	0.002	1	Mancozeb	F	1	1
Aldicarb Sulfoxide	M	0.002	1	Metalaxyl	F	0.084	0.5
Anilazine	F	0.15	1	Methamidophos	I	0.30	0.1 negligible
Atrazine	H	0.025	none	Methidathion	I	0.055	0.2
Azinphos-Methyl	I	0.009	0.3	Methomyl	I	0.002	0.2 negligible
Captan	F	0.075	25 interim	Methyl Parathion	I	0.058	0.1 negligible
Carbaryl	I	0.002	0.2 negligible	Metolachlor	H	0.045	0.2
Carbofuran	I	0.001	2	Mevinphos	I	0.15	0.25
Chlorothalonil	F	0.005	0.1	Myclobutanil	F	0.14	none
Chlorpropham	H	0.066	50	Omethoate	I	0.17	0.2
Chlorpyrifos	I	0.038	none	Oxamyl	I	0.002	0
Cypermethrin	I	0.20	none	Oxyfluorfen	H	0.045	none
DCPA	H	0.013	2	p,p'-DDE	M	0.013	1.0 revoked
Diazinon	I	0.016	0.1	p,p'-DDT	I	0.013	1.0 revoked
Dichloran	F	0.050	0.3	p,p'-Dicofol	I	0.22	none
Dichlorvos	I	0.033	none	Pendimethalin	H	0.035	0.1
Dieldrin	I	0.050	0.1	Pentachlorobenzene	O	0.013	not found
Dimethoate	I	-- ^b	0.2	Pentachloronitrobenzene	F	0.030	0.1 interim
Diphenylamine	F	0.014	none	cis-Permethrin	I	0.028	0.05
Disulfoton	I	0.10	0.75	trans-Permethrin	I	0.038	0.05
Endosulfan I	I	0.050	0.2 negligible	Phorate	I	0.042	0.5
Endosulfan II	I	0.060	0.2 negligible	Phosalone	I	0.045	0.1 negligible
Endosulfan Sulfate	M	0.075	0.2 negligible	Phosmet	I	0.044	0.1
Ethion	I	0.011	none	Phosphamidon	I	0.28	0.1
Ethoprop	I	0.035	0.2 negligible	Propamocarb	F	-- ^b	0.5
Ethyl Parathion	I	0.055	0.1 negligible	Propargite	I	0.050	0.1

continued on next page

Appendix B continued:

Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)	Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)
Ethylenebis Dithiocarbamate (EBDCs)	F	1	0.1 negligible	Simazine	H	0.035	none
Fenamiphos	I	0.2	none	Terbufos	I	0.025	none
Fenvalerate	I	0.070	0.02	Thiabendazole	F	2	10.0
Hexachlorobenzene	F	0.023	not found	Triadimefon	F	0.17	0.05 pending
Hexazinone	H	0.15	none	Trifluralin	H	0.013	0.5 negligible
Imazilil	F	2	none	Vinclozolin	F	0.038	0.1

^a F = Fungicide, H = Herbicide, I = Insecticide, M = Metabolite (break-down product), O = Other, *e.g.*, contaminant of the production process.

^b Unable to analyze.

Tart Cherries

Introduction

The red tart cherry, *Prunus cerasus*, is a perennial tree fruit related to the plum, peach, apricot, almond, and numerous other species of the north temperate zone. It is grown commercially for its tart fruit, which is primarily used in baking and cooking. Following planting, trees require an additional 5-8 years of care before producing fruit. Cherry orchards have an average economic life of 25-30 years, before a significant decline in yield and fruit quality, increasing disease problems, and tree death make the orchard operation inefficient and costly.

Michigan is the largest producer of tart cherries, harvesting 70 to 75% of the U.S. crop. Total tart cherry acreage in 1997 was 32,300 acres, representing 3,600,000 trees, which was down 9% from the previous 3 years. Oceana, Leelanau, and Grand Traverse remained the top three tart cherry counties. They accounted for more than 61% of the acres, up from 57% three years ago. The state produced 221 million pounds of cherries (8400 lbs/acre), with only 0.5% going to fresh market and the remainder processed (canned, frozen, other products). At 15.6 cents/lb, the total value of tart cherry production was \$34,380,000 in 1997.

Major Pests

Cherry Fruit Fly (*Rhagoletis cingulata*). Primary damage results from the feeding of the larva within the fruit. Infested fruits appear normal until the maggot is nearly full-grown, at which time sunken spots appear. Maggots and their frass (excrement) within the fruit render the product unsalable. There is a zero USDA tolerance for cherry fruit fly maggot in fruit. In addition, infested fruit are more susceptible to brown rot and other diseases. The flies are controlled with effective chemicals before the female matures and lays eggs.

Plum Curculio (*Conotrachelus nenuphar*). This weevil is one of the most important and destructive insects attacking tree fruits. Overwintering adult beetles attack the fruit soon after it forms, eating holes through the skin and feeding on the pulp. The female makes distinctive, crescent-shaped wounds on the skin when laying eggs. Plum curculio is capable of causing great damage and is considered a difficult pest to control.

Brown Rot (*Monilinia fructicola*). Brown rot is one of the most important diseases of stone fruits in the eastern United States. Field losses of tart cherries can be extensive if conditions favorable for disease development occur during the blossom period, following shuck fall, or during the preharvest and harvest period. The incidence of blossom blight caused by *M. fructicola* is directly related to temperature and duration of wetness, with as little as five hours of wetting needed at 77°F to cause significant infection. The disease causes lesions on the fruit; the lesions can expand rapid, and spread through fruit-to-fruit contact, resulting in significant yield losses. Tart cherry mummies remaining in the tree from the previous season can provide the primary inoculum for fruit rot the next year. Brown rot may also develop during storage and shipment if fruit are not handled properly during and after harvest.

Cherry Leaf Spot (*Coccomyces hiemalis*). This fungus mainly infects the foliage. The fungus overwinters in leaf debris, germinating during the next spring. About five to six hours of leaf wetness during optimal temperatures are sufficient to cause a light infection. Poorly controlled leaf spot can cause early defoliation of trees, resulting in reduced winter hardiness and even tree death.

Pesticides Used

1. Azinphos-methyl (Guthion)

Non-systemic, broad-spectrum organophosphate insecticide, used to control plum curculio and cherry fruit fly.

Oral LD₅₀ (rats) = 5 mg per kg body weight
 Dermal LD₅₀ (rabbits) = 220 mg per kg body weight

Persistence in soil dependent upon soil type, with a half-life of 5 days in sandy loam. On vegetation, the approximate residual period is 1-3 weeks
 15 day PHI
2. Carbaryl (Sevin)

Broad-spectrum, systemic, cholinesterase inhibitor, widest use of any insecticide, used to control several cherry insect pests.

Oral LD₅₀ (rats) = 307 mg per kg body weight
 Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Insecticidal properties on crop for 3-10 days. Half life in aerobic soil 7 days, anaerobic 28 days.
 3 day PHI
3. Chlorpyrifos (Lorsban)

Heterocyclic organophosphate contact poison, used to control lesser peach tree borer and American plum borer as trunk sprays.

Oral LD₅₀ (rats) = 135 mg per kg body weight
 Dermal LD₅₀ (rabbits) = 2000 mg per kg body weight

Moderately persistent but relatively immobile. The half-life ranges from 11-141 days depending on soil type, soil pH, and aerobic conditions.
 6 day PHI
4. Permethrin (Ambush, Pounce)

Broad-spectrum synthetic pyrethroid insecticide. Used to control green fruitworm, plum curculio, and cherry fruit fly.

Oral LD₅₀ (rats) > 4000 mg per kg body weight
 Dermal LD₅₀ (rabbits) > 4000 mg per kg body weight

Breaks down quickly in the environment and on vegetation, allowing for short pre-harvest intervals.
 3 day PHI
5. Phosmet (Imidan)

Non-systemic, organophosphate insecticide. Used to control plum curculio, leafrollers, and cherry fruit fly.

Oral LD₅₀ (rats) = 147 mg per kg body weight
 Dermal LD₅₀ (rabbits) = 3160 mg per kg body weight

Half-life in sandy loam soil 3-19 days, with increasing rates of breakdown in higher pH
 7 day PHI
6. Captan

Non-systemic sulfenimide fungicide, used in combination with other fungicides to control brown rot and leaf spot.

Oral LD₅₀ (rats) = 9000 mg per kg body weight
 No dermal irritation

Half-life in soil 1-10 days, with activity on potato foliage for 23d

0 day PHI. May be used as a post-harvest treatment on cherries.

7. Chlorothalonil (Bravo)

Substituted aromatic, very useful, broad-spectrum foliage-protectant fungicide, used to control brown rot and leaf spot.

Oral LD₅₀ (rats) > 10,000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 10,000 mg per kg body weight

“Fairly persistent” on crop surfaces. Half-life in aerobic soils 1-3 months

PHI: Do not apply after shuck split and before harvest

8. Dodine (Sylit)

A guanidine fungicide, used to control cherry leaf spot and brown rot. It has disease specificity and slight systemic qualities.

Oral LD₅₀ (rats) = 1000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 1500 mg per kg body weight

0 day PHI

9. Fenbuconazole (Indar)

A systemic fungicide with curative and protective qualities. Used to control brown rot, powdery mildew, and leaf spot.

Oral LD₅₀ (rats) > 2000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 5000 mg per kg body weight

0 day PHI

10. Iprodione (Rovral)

Dicarboximide fungicide with preventative and curative action. Used to control brown rot and leaf spot.

Oral LD₅₀ (rats) = 3500 mg per kg body weight

Dermal LD₅₀ (rabbits) > 1000 mg per kg body weight

Half-life in soil is 20-160 days

7 day PHI

11. Myclobutanil (Nova)

A systemic fungicide with curative and protective qualities. Used to control brown rot, powdery mildew, and leaf spot.

Oral LD₅₀ (rats) = 1600 mg per kg body weight

Dermal LD₅₀ (rabbits) > 5000 mg per kg body weight

7 day PHI

12. Sulfur

One of the oldest effective fungicides known, both systemic and non-contact, used to control blossom brown rot and fruit brown rot.

Oral LD₅₀ (rats) > 5000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 5000 mg per kg body weight

PHI: Exempt

13. Tebuconazole (Elite)

A systemic fungicide with curative and protective qualities. Used to control brown rot, powdery mildew, and leaf spot.

Oral LD₅₀ (rats) = 4000 mg per kg body weight

Dermal LD₅₀ (rabbits) > 5000 mg per kg body weight

0 day PHI

Materials and Methods—see Appendix A

Grower and Experimental spray application timelines—see Figure 1

Results

A total of 33 cherry samples were examined for residues, 21 from commercial orchards and 12 from research plots at Michigan State University. All samples were tested for a total of 65 pesticides and metabolites (Appendix B). Seven different pesticides were detected, three in samples from research plots and seven in orchard samples. No residues were detected for the additional pesticides listed in Appendix B. It is important to note that it is currently standard commercial practice to harvest tart cherries into water, rinsing the fruit prior to going to the processor.

Organophosphates were used by all of the growers. The samples were all tested for chlorpyrifos (Appendix B), but no residues of this product were found; this product is used to control American plum borer and peach tree borer, and was used by five of the seven growers (Table 2a). The shortest pre-harvest interval used by the growers was 56 days (labeled PHI = 6 days), which could account for the lack of detectable residue. Azinphos-methyl is used for control of cherry fruit fly by four growers (Table 2a). It was detected in the off-tree samples from only two of these growers. It was not detected after washing, though it was detected in one sample that was processed. Methyl parathion was used by one grower (Fig. 1), with no residues detected (Table 2a). In the experimental plots, Spinosad was used to control cherry fruit fly without the use of organophosphates; consequently, no organophosphates were detected from these samples.

Phosmet was used by four of the growers, and interestingly, more likely used by those growers who did not use azinphos-methyl. Phosmet was only detected on two growers' samples (Table 2a). Both of these growers (#1 and #6) did use phosmet (Table 2a, Fig. 1). There were two other growers (#2 and #4) who also used phosmet, but applied a lower total amount per acre (Fig. 1); no residue was found on samples from their orchards. In both cases of positive detections, the off-tree sample was only 0.2 ppm, which was 50-fold less than current tolerance. When the Grower #6 sample was washed, phosmet was no longer detected. When the sample from Grower #1 was washed, the level of phosmet decreased to 0.04 ppm, now 250-fold less than tolerance. Finally, there was no residue detected in the processed product (Table 2a).

Grower #2 provided the only recorded use of carbaryl (Fig. 1), and it was detected in the off-tree sample at limits below quantification (Table 2a). It was also detected in the off-tree sample from Grower #7 (Table 2a), who did not record carbaryl use (Fig. 1). Carbaryl was not applied to the experimental plots, yet was detected in all but one sample from these plots (Table 2b). In all cases, the amounts recovered were below quantifiable limits.

Permethrin was detected in five samples (Table 2a) from three growers, yet only two growers reported using this product (Fig. 1). Residues in Grower #5's samples did not change with washing and processing. Given the short persistence on vegetation for this product and the short PHI, it was surprising to find this product on the fruit four weeks after the last application in the orchard (Fig. 1). Grower #2 applied permethrin one time, 64 days before harvest, with residue detected only in the processed sample. Permethrin was also detected in the washed fruit from Grower #6, who did not report using this product. The residue found was 15-fold less than tolerance (Table 2a).

Chlorothalonil was used in all but one of the seven orchards (Fig. 1), with residues detected only in the processed sample from Grower #2. Growers # 3, 4, and 7 used

chlorothalonil from 8-10 weeks prior to sampling (Fig. 1), but no residues were detected in the cherries (Table 2a). Grower #2 had detectable residues in the processed sample, 10-fold less than tolerance. Chlorothalonil was found in seven of the 12 experimental plots (Table 2b), with applications having been made eight weeks prior to sampling (Fig. 1). All plots were treated the same for all chemicals except Spinosad (Fig. 1).

Captan was used by three of the growers (Table 2a), yet it was only detected in samples taken from Grower #7; washing reduced residues from 0.4 to 0.08 ppm (Table 2a); the residue in the processed samples was 0.03 ppm. The amount of residue detected was from 250- to 1250-fold less than tolerance (Table 2a). Although captan had not been applied to the experimental plots, there was one sample with a detection of 0.1 ppm (Table 2b).

Iprodione was detected when it was used (Fig. 1, Table 2a). Samples taken from Grower #5 had residue on all three samples, off-tree, washed, and processed, with the amounts decreasing respectively (Table 2a). Grower #6 used less iprodione and with twice the pre-harvest interval, with residue found only on the off-tree sample.

Grower Interviews. Most of the cherry growers were following a middle-range IPM program. In other words, their orchards were being scouted, and the growers were using weather-based disease forecasting. As a result, most sprays were applied only in response to indications that insect or disease problems were imminent.

In general the growers were very satisfied with these middle-range IPM techniques. In fact, they do not see these techniques as experimental; for them, these methods are “business as usual.” Most of the growers felt that the IPM approach saved them time, because they applied fewer sprays than they would have if they were following a spray calendar. One grower, however, felt that IPM might require more time because a good scouting program could identify a need for a spray that the spray calendar would not have called for: *“a scout’s job and reputation are on the line.”*

Most of the growers hire a scouting service that provides them with a weekly report on current and emerging pest problems. The service provides a report on pest levels, with the scouting service recommending some management action in some cases. One scout is encouraging the grower to manage tree nutrition as a way of managing pests. Most of the growers were satisfied with their scouting service. *“A scout is another set of eyes to alleviate some worries about pest control.” “A scout is an expense, but they lessen the stress.”*

Most of the growers felt that the IPM approach saved them money. *“It saves money because I don’t have to buy spray [materials]...I can hold off on sprays or don’t have to spray at all...It’s \$1,000 to pay a scout but it’s worth it because I save money in long run...in chemicals,...fuel, and time.”* One grower noted that savings were dependent on the weather, because when weather conditions were conducive to insect or disease problems, more applications of pesticides were required.

The growers generally felt that the IPM techniques were better for the environment. Several growers noted there were no observed changes in the flora and fauna of the landscape during the growing season. *“We’re putting less chemicals out there...it benefits us all, including neighbors and the environment.” “We don’t hurt [the environment]...I should get paid [a lot] for my wildlife, we have [a lot] of deer and fish.”*

In general the growers felt that the IPM techniques were better for the health of consumers and of people working on the farm. *“If there [are] not as many chemicals, then there is no residue.” “Hopefully less chemicals will be healthy for the consumer...I’m not a scientist and*

can not speak to that...I believe it is.” Several growers are regularly checked for blood levels of the active ingredients in pesticides. “I’ve had blood tests before and after and always been clean.” “We use masks and gloves...I don’t like spray...I wish they would prove if it is harmful or not...we had blood test[s], nothing came out of it, there was nothing bad or wrong.” Another grower did not see that IPM had made any difference in personal health. “It’s a big concern...you don’t know...we use a cab [on the sprayer] and mask[s]...we’d tolerate more damage [in the produce] if people [consumers] would accept it.”

Finally, the cherry growers were generally very satisfied with the quality and quantity of production using the IPM techniques. One grower said that no load of fruit had ever been rejected, and that the fruit always received the highest grade. Another grower said that the IPM approach made it possible to put bees in the orchard, which increased the yield of cherries.

Discussion

During the 1998 growing season, our sample of seven tart cherry growers in the northwestern region of Michigan utilized pesticides based on 13 different active ingredients to control four major insect and fungal pests. Applications were generally made at less than half of the label rate, and pre-harvest intervals were generally more than double the label limit. Across the 33 samples, 31 residues of seven products were detected. More than one-third of these were below quantifiable limit, and all were less than ten percent of the current tolerance.

The analysis of residues in the samples did reveal several anomalous results. These include the detection of residues at later stages (e.g., processing) when they had not been detected at earlier stages (e.g., off-tree or washing), and the detection of residues of an active ingredient that had not been used by the grower. Since each grower’s results are based on three separate random samples, the former anomaly might be due to sampling variability. The detection of residues of an active ingredient that had not been used by a grower might be due to a number of factors, such as residual pesticide in a spray tank or spray drift, or to contamination in the washing and processing stages. We are continuing to investigate the possible sources of these anomalies, and will explore further the possible causes during the coming growing season.

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Table 1. Summary of Insecticides and Fungicides Registered for Use on Tart Cherries.

Common Name	Trade Name	Type ¹	Common Name	Trade Name	Type ¹
<i>Used during 1998 ²</i>			<i>Not used in 1998 ²</i>		
azinphos-methyl	Guthion	OP	diazinon	Spectracide	OP
carbaryl	Sevin	Carb	endosulfan	Thiodan	OC
chlorpyrifos	Lorsban	OP	esfenvalerate	Asana XL	O
iprodione	Rovral	O	fenbutatin-oxide	Vendex	O
methyl parathion	PennCap-M	OP	clofentezine	Apollo SC	O
permethrin	Ambush	O	fenarimol	Rubigan	O
phosmet	Imidan	OP	propiconazole	Orbit	O
captan	Captan	O	vinclozolin	Ronilan	O
chlorothalonil	Bravo	B2			
dodine	Syllit	O			
fenbuconazole	Indar	O			
myclobutanil	Nova	O			
sulfur		O			
tebuconazole	Elite	O			

¹ B2 = B2 carcinogen; Carb = carbamate; OP = organophosphate; OC = Organochlorine; O = other category.

² Refers to pesticides used by Michigan growers in this study.

Table 2a. Potential and actual product use in tart cherries, 1998, with pre-harvest intervals and residue found.

Product	n ^a	Maximum Rate ^b	Actual Total Use (rate X #app)		PHI ^c (days)	Actual PHI (days)		Tolerance (ppm)	Residue Results			
			Mean	Range		Mean	Range		No. (%) Positive Samples	Mean (ppm)	Range (ppm)	
phosmet	4	12.5 lb	4.1 lb	2-9	7	21	15-26	10	3 (14.3)	0.15	0.04-0.2	
Off tree									2 (9.5)	0.20	0.20	
Washed									1 (4.8)	0.04	0.04	
Processed									0	--	--	
methyl parathion	1	36 pt	6 pt	--	14	27	--	1	0	--	--	
Off tree									--	--	--	
Washed									--	--	--	
Processed									--	--	--	
permethrin	2	76.8 oz	15.6 oz	9.6-21.6	3	49	34-64	3	5 (23.8)	0.12	0.03-0.2	
Off tree									1 (4.8)	0.20	0.20	
Washed									2 (9.5)	0.08	0.05-0.1	
Processed									2 (9.5)	0.12	0.03-0.2	
carbaryl	1	17.5 lb	4 lb	--	3	38	--	10	2 (9.5)	BQL^d	BQL	
Off tree									2 (9.5)	BQL	BQL	
Washed									0	0	--	
Processed									0	0	--	
captan	3	28 lb	6.5 lb	2-10	0	43	16-77	100	3 (14.2)	0.26	0.08-0.4	
Off tree									1 (4.8)	0.4	--	
Washed									1 (4.8)	0.08	--	
Processed									1 (4.8)	0.3	--	
azinphos-methyl	4	6 lb	4.4 lb	2-6.5	15	36	16-70	5	3 (14.2)	0.15	0.1-0.2	
Off tree									2	0.1	0.1	
Washed									0	--	--	
Processed									1	0.2	--	
iprodione	2	8 lb	2.1 lb	0.64-3.6	7	11	6-15	20	4 (19)	0.38	0.1-0.8	
Off tree									2 (9.5)	0.65	0.5-0.8	
Washed									1 (4.8)	0.1	--	
Processed									1 (4.8)	0.1	--	
chlorothalonil	6	20 lb	4.3 lb	3-6	<i>Shuck split</i>	65	61-71	0.5	1 (4.8)	0.04	--	
Off tree										0	--	--
Washed										0	--	--
Processed										1 (4.8)	0.04	--

^aNumber of growers who recorded application of product during 1998.

^bBased on 1998 product label.

^cLabeled pre-harvest interval, expressed in days.

^dBQL, below quantifiable limit.

Table 2b. Total product used in experimental plots in 1998, with pre-harvest interval and residue found.

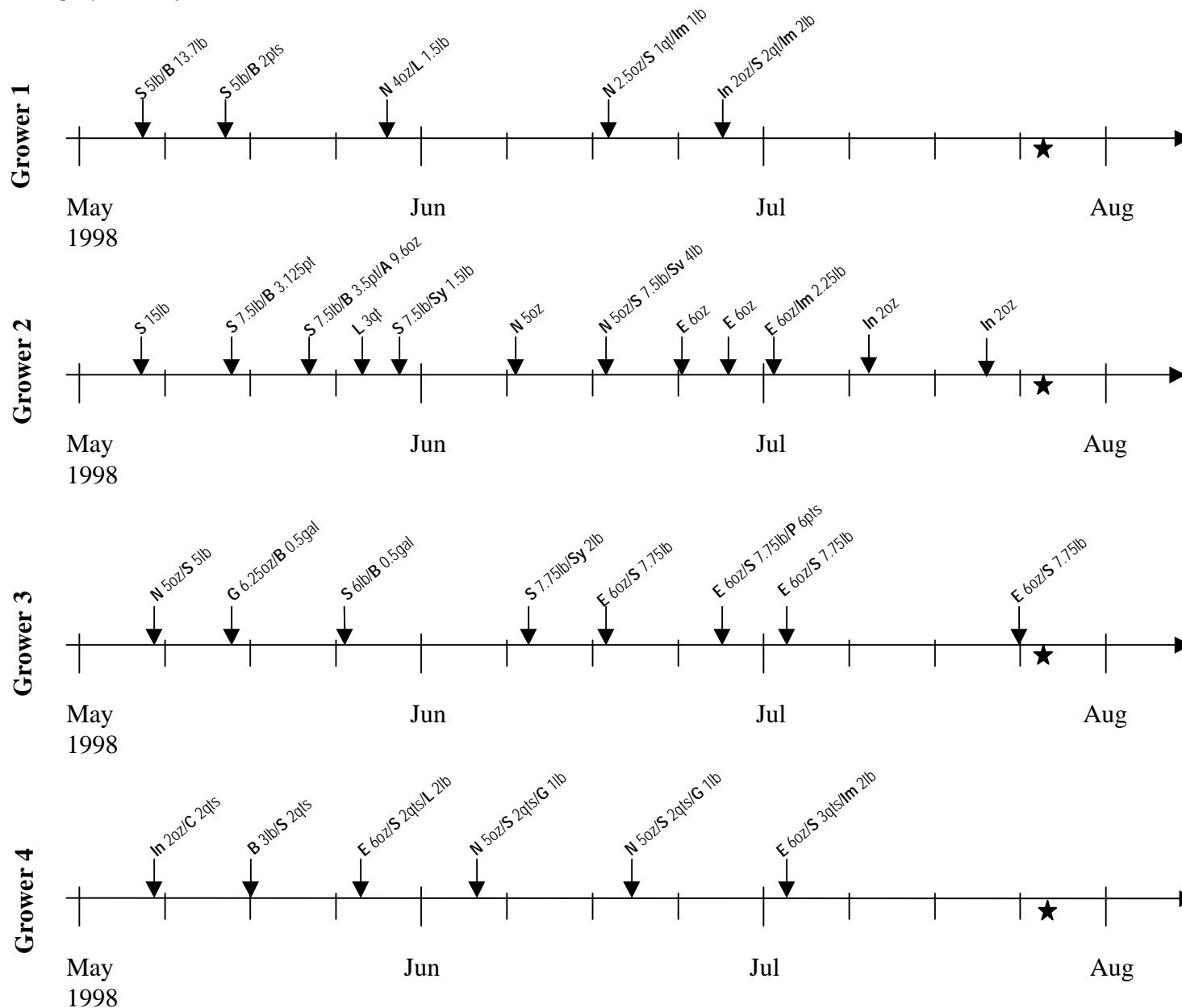
Product	<i>n</i> ^a	Total Used (rate x #app)		PHI (in days) ^b		Tolerance ppm	Residue Results		
		Mean	Range	Mean	Range		No. (%) Positive Samples	Mean ^c (ppm)	Range (ppm)
phosmet	0	--	--	--	--	10	0	--	--
methyl parathion	0	--	--	--	--	1	0	--	--
permethrin	0	--	--	--	--	3	0	--	--
carbaryl	0	--	--	--	--	10	11 (92)	BQL	BQL
captan	0	--	--	--	--	100	1 (8.3)	0.1	--
azinphos-methyl	0	--	--	--	--	5	0	--	--
iprodione	0	--	--	--	--	20	0	--	--
chlorothalonil	12	3 lb	3	61	61	0.5	7 (58.3)	0.02	0.009-0.03

^aNumber of plots where product was applied during 1998.

^bPre-harvest interval, expressed in days.

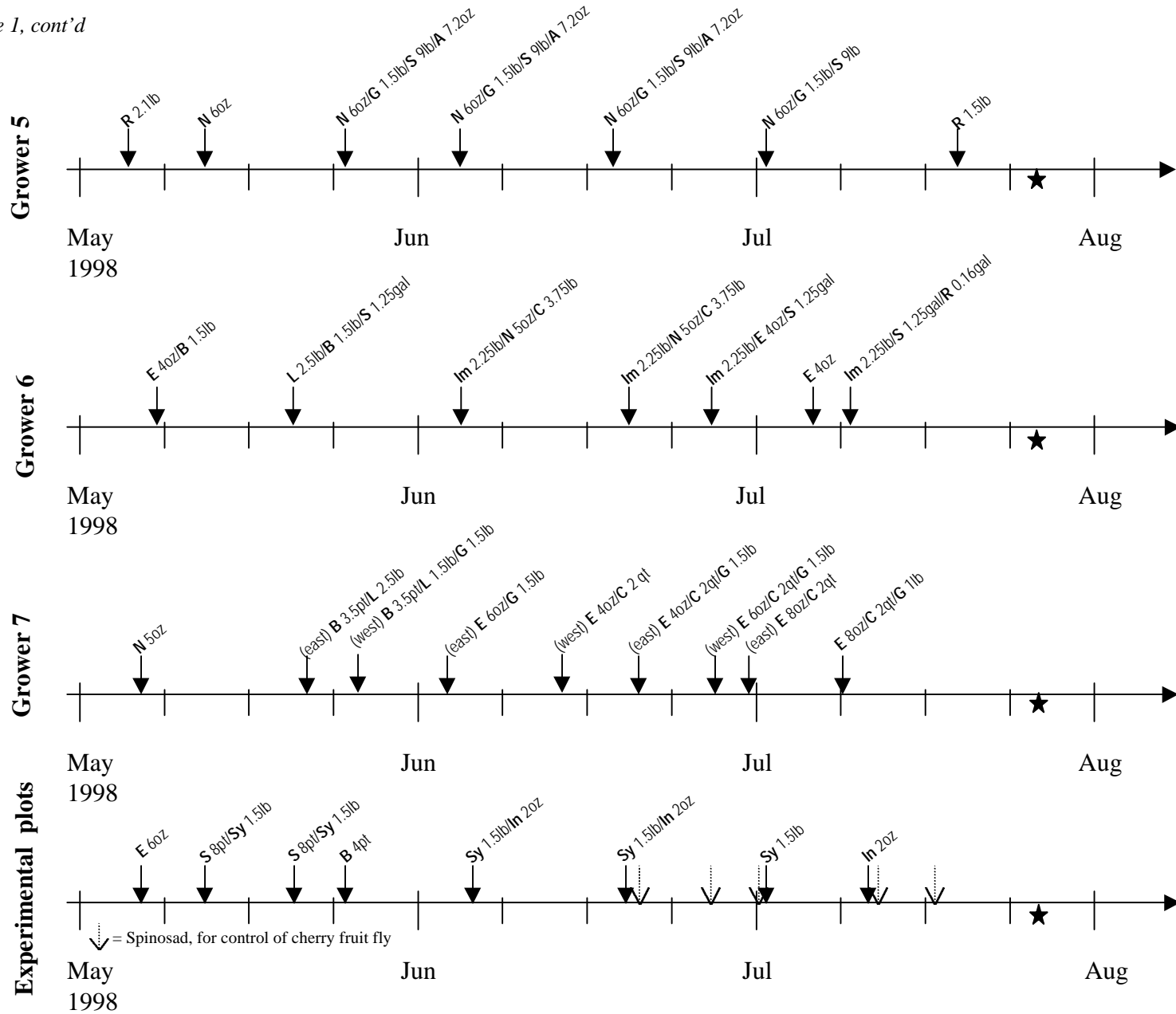
^cBQL, below quantifiable limit.

Figure 1. Grower spray records for tart cherries, 1998



↓ = Pesticide application. A = Ambush, B = Bravo, C = Captan, E = Elite, G = Guthion, Im = Imidan, In = Indar, L = Lorsban, N = Nova, P = Penncap, R = Rovral, S = Sulfur, Sv = Sevin, Sy = Syllit. Product amounts per acre.
 ★ = Date samples taken

Figure 1, cont'd



↓ = Pesticide application. A = Ambush, B = Bravo, C = Captan, E = Elite, G = Guthion, Im = Imidan, In = Indar, L = Lorsban, N = Nova, P = Penncap, R = Rovral, S = Sulfur, Sv = Sevin, Sy = Syllit. Product amounts per acre. Products applied after harvest date not listed.

★ = Date samples taken

Appendix A – Materials and Methods

Harvest and handling

A. Research samples

The research plots of tart cherries (variety ‘Montmorency’) were located at the Northwest Michigan Horticultural Research Station (NMHRS) in Leelanau County, Michigan. The NMHRS staff conducted insecticide trials for the control of cherry fruit fly during the 1998 growing season. The trials tested several different timings of spinosad (SpinTor®; metabolite from fermentation of the bacterium *Saccharopolyspora spinosa*) versus plots not treated with an insecticide. The Department of Agriculture laboratory did not have the ability to test for spinosad. However, samples from each plot were analyzed for fungicides. The fungicide treatments were identical for all plots. Pesticides used and the timing of applications are in Figure 1; since residue analysis was not performed for spinosad, all treatments were combined into one timeline.

Approximately 10 lbs. of cherries per sample were harvested by hand on 24 July 1998. Each sample was individually flushed with well water for three hours to simulate the rinsing performed on commercially harvested cherries and to cool and harden the fruit before pitting. Each sample was pitted separately, and the pitting machine was rinsed with well water between samples. The pitted cherries were placed in a plastic bag and then stored in the freezer (10°F) until residue analysis.

B. Grower samples – fresh, unrinsed:

Seven Michigan tart cherry growers participated in this study. Pesticides used and the timing of applications are in Figure 1. Approximately 10 lbs. of cherries were sampled from each grower. The samples were taken directly from the mechanical harvesters, before the fruit was rinsed. Each sample was stored in a 35°F cooler for ≈ 12 hours to cool and harden the fruit pitting. Each sample was pitted and stored in the freezer (10°F) until residue analysis.

C. Grower samples – fresh, rinsed:

Water-rinsed cherry samples (approximately 10 lbs. each) were taken from the same seven growers mentioned above. The samples were taken directly from water-filled tanks at one of two different processing plants. The tanks were held in a low temperature cooler until processing. Each sample was pitted and stored as described above.

D. Grower samples – processed:

Canned cherry samples were taken from each of the seven growers mentioned above. Approximately 10 lbs. of cherries were collected at the very last stage of processing, just before sugar was added and the cans were sealed. The processing steps (rinse, shake, rinse, flume, sort, and pit) were similar for processors A and B. Both the processed and rinsed (described above) samples were taken from the same tanks. Each sample was placed in a plastic bag and stored in the freezer (10°F) until residue analysis.

Grower Interviews

Interviews were conducted by the Department of Sociology, Michigan State University. Personal interviews of 90 minutes were conducted with each of the tart cherry growers who participated in this study, after the conclusion of fall harvest, and at a time and place convenient for each grower. The interview began with a question about the grower's general satisfaction with the pest management method that had been used during the 1998 growing season. The interview then proceeded to explore the grower's satisfaction with specific aspects of the pest management method (monetary cost, operator and labor time, investment, environmental impacts, consumer and grower/labor health impacts, and quantity and quality of production). The interview concluded with questions about the grower's sources of information concerning pest management. Because of the small number of growers in this commodity group, the responses were not analyzed statistically, but were summarized, with illustrative quotations where appropriate.

Pesticide Residue Analysis:

The Laboratory Division of the Michigan Department of Agriculture performed the residue analysis.

- I. The samples arrived in the laboratory frozen. They were stored in a freezer, then thawed prior to grinding and extraction.
- II. Preparation of the sample followed Section 102 of the Pesticide Analytical Manual (1997, Vol. 1, 3rd edition, U.S. Dept. of Health and Human Services, Public Health Service, Food and Drug Administration, pp.102-1—102-3). None of the samples were washed prior to analysis. The whole submitted cherry sample was used after discarding stems and pits.

- III. The extraction method used for most of the compounds was the “Luke II modified Extraction Screening Method for Pesticide Residues in Non-Fatty, High-Moisture Foods.” This is a modification of the “Acetone Extraction Screening Method for Pesticide Residues in Non-Fatty, High Moisture Foods,” (Pesticide Analytical Manual, 1997, Vol. I, Sect. 302, U.S. Dept. of Health and Human Services, Food and Drug Administration). This is a multi-residue method for the analysis of organohalogen, organonitrogen, organophosphate, organosulfur, and carbamate pesticide residues in nonfatty, high moisture matrices, and returns both quantitative and qualitative results. Analysis of all the compounds except the carbamates was by Gas Chromatography/Mass Spectroscopy (GC/MS). Analysis of the carbamates was by Liquid Chromatography/Post-Column Derivatization/Fluorescence Detection, with confirmation by MS.
- IV. The extraction and analysis method used for Benomyl was from “HPLC Fluorometric Analysis of Benomyl and Thiabendazole in Various Agricultural Commodities” (Bulletin #3650, E. J. Wojtowicz)
- V. Dithiocarbamates were analyzed using the Lowen and Pease method (G. Zweig [Ed.], 1964. Analytical methods for Pesticides, Plant Growth Regulators, and Food Additives, p. 65. *In* Fungicides, Nematocides and Soil Fumigants, Rodenticides, and Food and Feed Additives, Vol. III, Academic Press).
- VI. Limits of Detection were originally set by analyzing a set of spikes at or near the believed limit of detection. The standard deviation was determined and multiplied by the student’s T, at the 99% confidence level, to calculate the limit of detection. If the calculated limit of detection appeared excessively low or high, a set of spikes was analyzed at a level thought to be more realistic, based on the signal to noise ratio. If all of these new spikes were detected and confirmed, then this became the new limit of detection. These were determined in one commodity and then assumed to be the same in other commodities unless spike recovery data indicated otherwise.
- VII. Tolerances were from Duggan (1998, Pesticide Chemical News Guide, CRC Press LLC).

Appendix B—Complete list of pesticides included in the residue analysis of all tart cherry samples.

Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)	Compound	Type ^a	Limit of Detection (ppm)	Tolerance (ppm)
3-Hydroxycarbofuran	M	0.002	none	Imazilil	F	2	none
Acephate	I	0.63	none	Iprodione	F	0.065	20
Alachlor	H	0.019	none	Lindane	I	0.063	1
Aldicarb	I	0.001	none	Malathion	I	0.17	8
Aldicarb Sulfone	M	0.002	none	Methamidophos	I	0.30	none
Aldicarb Sulfoxide	M	0.002	none	Methidathion	I	0.045	0.05
Anilazine	F	0.15	none	Methomyl	I	0.002	none
Atrazine	H	0.025	none	Methyl Parathion	I	0.058	1
Azinphos-Methyl	I	0.09	2	Metolachlor	H	0.045	0.1
Captan	F	0.075	100	Mevinphos	I	0.15	none
Carbaryl	I	0.005	10	Myclobutanil	F	0.14	5
Carbofuran	I	0.001	none	Oxamyl	I	0.002	none
Chlorothalonil	F	0.005	0.5	Oxyfluorfen	H	0.045	0.05
Chlorpropham	H	0.066	none	p,p'-DDE	M	0.013	0.2
Chlorpyrifos	I	0.038	1	p,p'-DDT	I	0.013	0.2
Cypermethrin	I	0.20	none	p,p'-Dicofol	I	0.22	5
DCPA	H	0.013	none	Pendimethalin	H	0.035	none
Diazinon	I	0.016	0.75	Pentachlorobenzene	O	0.013	not found
Dichloran	F	0.050	20	Pentachloronitrobenzene	F	0.030	none
Dichlorvos	I	0.033	none	<i>cis</i> -Permethrin	I	0.028	3
Dieldrin	I	0.050	0.03	<i>Trans</i> -Permethrin	I	0.038	3
Diphenylamine	F	0.014	none	Phorate	I	0.042	none
Disulfoton	I	0.10	none	Phosalone	I	0.045	15
Endosulfan I	I	0.050	2	Phosmet	I	0.044	10
Endosulfan II	I	0.060	2	Phosphamidon	I	0.28	none
Endosulfan Sulfate	M	0.075	2	Propargite	I	0.050	none
Ethion	I	0.011	0.1	Simazine	H	0.035	0.25
Ethoprop	I	0.035	none	Terbufos	I	0.025	none
Ethyl Parathion	I	0.055	1	Thiabendazole	I	2	none
Fenamiphos	I	0.2	0.25	Triadimefon	I	0.17	none
Fenvalerate	I	0.070	10	Trifluralin	H	0.013	0.05
Hexachlorobenzene	I	0.023	not found	Vinclozolin	F	0.038	25
Hexazinone	H	0.15	none				

^aF = Fungicide, H = Herbicide, I = Insecticide, M = Metabolite (break-down product), O = Other, *e.g.*, contaminant of the production process.