Potential for Zero Residue Disease Control Programs for Fresh and Processed Apples Using Sulfur, Fenarimol, and Myclobutanil

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ABSTRACT

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In 1990 and 1991, efficacy of disease control and fungicide residues in raw and processed products were evaluated for spray programs for scab (*Venturia inaequalis*) and sooty blotch (*Gloeodes pomigena*) on three cultivars of apple (*Malus* × *domestica*). Spray programs based exclusively on fenarimol and myclobutanil resulted in suboptimum control of fruit scab and no control of sooty blotch. A spray program of sulfur and one consisting of tebuconazole plus captan resulted in good and excellent control of apple scab, respectively. Both programs provided adequate control of sooty blotch. Residues of fenarimol and myclobutanil in unwashed raw apples and in frozen slices, sauce, and juice concentrate made from washed and peeled apples were far below tolerance levels established by the Environmental Protection Agency. Increasing the interval between the last spray and harvest reduced but did not eliminate residues in processed products. Residues of sulfur were high in unwashed fruit, but at or below detection limits in frozen slices, sauce, and juice made from washed and peeled fruit.

As a result of the large number of pathogens and arthropod pests that attack apple (*Malus* × *domestica* Borkh.) and its low tolerance for damage, more pesticides are used per hectare on this crop than on any other crop in Michigan. Eight to 12 fungicide treatments are applied each growing season to prevent losses from apple scab, caused by *Venturia inaequalis* (Cooke) G. Wint.; and in some seasons fungicide sprays are required to prevent losses from sooty blotch, caused by *Gloeodes pomigena* (Schwein.) Colby. Because of the high rainfall and moderate temperatures that exist in Michigan and in most northeastern states, apple scab would destroy the crop on most present cultivars if they were not sprayed with fungicides. Although several disease management programs have been designed to help growers reduce the number of fungicide applications per season (4,6,8,9,17), none have documented the fungicide residues on the raw and processed products that result from the use of these programs.

How strictly the Environmental Protection Agency (EPA) will enforce the Delaney clause, which requires that no substance known to be carcinogenic to humans or animals shall be added to processed foods, will affect which pesticides growers use for pest control on apples. Full enforcement of the zero cancer risk application of the law could lead to cancellation of many commonly used fungicides (2). Disease control strategies which enable fruit growers to produce apples with fungicides with no known carcinogenic activity and with no or very low residues of fungicides at harvest would help to ensure safety to consumers, public confidence in apples and apple products, and long-term stability of the apple industry.

Currently, the processing industry is designing strategies for avoiding detectable pesticide residues in products made from apples. Processors ask growers to use pesticides known to disappear during processing or advise them to use intervals between last applications and harvest that give time for the pesticide residues to dissipate. Our study was undertaken to evaluate apple scab control strategies that utilize fungicides not currently classified as possible or probable human carcinogens by EPA (1,2). In addition, we determined the level of residues remaining in raw fruit and processed products.

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MATERIALS AND METHODS

Orchard applications. The experiment was conducted in 1990 and 1991 in a block of 7-yr-old trees on M7a rootstock located at the Botany and Plant Pathology Research Farm, Michigan State University, East Lansing. Treatments were applied to four replicate three-tree plots with one tree each of McIntosh, Delicious, and Golden Delicious. Each plot was separated from the next one in the row by a buffer plot, and from plots in adjacent rows by a buffer row. Treatments were arranged in a randomized complete-block design. Unsprayed plots from 1990 were replaced in 1991 with previously sprayed plots and the plots re-randomized. Buffer rows were sprayed on 23 April 1990 with 22.4 kg a.i./ha captafol (Difolatan 80DG) and on 17 April 1991 with a mixture of 140 g a.i./ha myclobutanil (Nova 40W) and 841 g a.i./ha benomyl (Benlate 50W) to delay the spread of scab from buffer trees to treatment trees.

Sulfur (Microthiol Special 80DF), fenarimol (Rubigan 1EC), myclobutanil (Nova 40W), tebuconazole (Elite 45DF), and captan (Captan 50W) were applied with a power takeoff air-blast sprayer built from a John Bean sprayer manifold delivering 748 L ha^{-1} of spray suspension at a pressure of 2,068 kPa. The tebuconazole-captan mixture was included to demonstrate that scab control was possible under the severe disease pressure encountered during the course of this study. The preharvest interval for fruit of Delicious and Golden Delicious was 18–33 days longer than for fruit of McIntosh. Concentrations of fungicides and spray dates are given in Tables 1 and 2.

Sampling and harvesting the fruit. At the time of optimum maturity for each cultivar, 18 fruit for the raw fruit residue analyses were collected at a height of 1.5–2.0 m above ground and from the inside and outside regions of each tree. The samples were frozen in plastic bags at −20 C within 4 hr after harvest. The remaining fruit on each tree were harvested into preweighed and labeled field crates. Yields were determined by weighing the fruit collected from each tree and were expressed as kg/cm^2 of trunk diameter at 25 cm above ground. Fruit of Golden Delicious were hand thinned in late July 1990. Fruit of other cultivars in 1990 and none of the fruit in 1991 were thinned.

Fruit processing. Fruit from all four replicates were combined into a composite sample of two to three field crates per treatment for processing as frozen slices, sauce, juice, and juice concentrate. Apples not processed on the day of harvest were held at 3 C prior to processing, which was always done within 3 days. Fruit were washed in cold, flowing tap water for 5 min then drained for 2–4 min. Apples for frozen slices and sauce were cored, peeled, and sliced with pilot scale commercial peeling and slicing equipment; then the slices were dipped in a

0.1% sodium metabisulfite solution to prevent discoloration. Samples for frozen slices were placed in labeled plastic bags, sealed, and frozen immediately. Slices for sauce manufacture were placed on stainless steel trays and steamed for 6–9 min (slice temperature 96–99 C for 3–4 min). The cooked slices were discharged into a Langsencamp pulper with a 1.5 mm screen operating at approximately 1,000 rpm. The hot apple sauce was put into plastic bag lined containers, sealed, and frozen. Washed apples for juice processing were macerated in a stainless steel hammer mill. The macerated pomace was placed on press cloths and pressed in a laboratory model hydraulic press. Juice was collected in plastic containers and frozen immediately. Approximately 1 mo later, portions of each frozen juice sample were removed from the freezer, thawed, and concentrated under vacuum to 70–72 Brix (approximately sevenfold concentration). After each sample was processed, the processing equipment was thoroughly cleaned to avoid cross contamination of samples with residues.

Analytical procedures. Myclobutanil and fenarimol residues were determined using modifications of methods received from Rohm and Haas Company (11) and DowElanco and Company (10), respectively. To determine myclobutanil, 20-g samples of apple flesh, sauce, or frozen slices were ground or blended for 4 min with 5 g of Celite and 100 ml of 0.1 N NaOH in methanol. Extracts were vacuum filtered and partitioned (twice) by shaking in a separatory funnel with 30 ml of 2% NaCl and 100 ml of methylene chloride. A 50–100 ml juice sample was extracted with 3–20 ml portions of methylene chloride. The methylene chloride extracts were percolated through anhydrous Na_2SO_4, which was then washed with 25 ml of methylene chloride, evaporated to dryness with a rotary vacuum at 45 C, and redissolved in toluene.

To determine fenarimol residues, 25-g samples of apple flesh, sauce, or frozen slices were shaken for 10 min with 60 ml of methanol. The methanol was filtered, then partitioned by shaking in a

Table 1. Incidence of scab and sooty blotch and yield of apple trees sprayed with sulfur or sterol demethylation inhibitor fungicides in 1990

Fungicide (a.i./ha)	Primary scab on McIntosh (%)		Fruit scab at harvest (%)				Sooty blotch (%) on Golden Delicious	Fruit yields by cultivar (kg/cm² of trunk diameter)		
	Spurs 1 June	Terminals 25 June	McIntosh 10 September	Delicious 28 September	Golden Delicious 11 October	Mean	11 October	McIntosh	Delicious	Golden Delicious
Sulfur 22.4 kg[w]	12.4 b[x]	17.4 b	16.1 d	13.3 c	4.7 d	11.3 d	31.3 c	0.62 a	0.50 c	1.39 a
Myclobutanil 140.2 g[w]	0.0 c	0.1 c	38.7 c	5.7 c	8.6 cd	17.8 cd	92.2 ab	0.83 a	0.87 abc	1.15 a
Myclobutanil 224.3/140.2 g[y]	0.0 c	0.0 c	46.7 c	13.1 c	12.5 bcd	24.1 c	90.5 ab	0.58 a	0.88 abc	1.03 ab
Fenarimol 52.6 g[w]	0.0 c	0.7 c	76.4 b	40.1 b	25.2 b	47.2 b	90.6 ab	0.79 a	0.90 ab	1.03 ab
Fenarimol 105.2/52.6 g[y]	0.0 c	0.3 c	67.4 b	52.5 b	20.4 bc	46.8 b	65.5 b	0.67 a	0.94 a	1.12 a
Tebuconazole 189.2 g + captan 2.24 kg[w,z]	0.0 c	0.0 c	3.2 d	2.5 c	1.4 d	2.4 e	11.8 c	0.91 a	1.22 a	1.20 a
Unsprayed control	28.2 a	72.0 a	100.0 a	100.0 a	96.6 a	98.9 a	100.0 a	0.05 b	0.52 bc	0.72 b
Cultivar means			49.7 A	32.4 B	24.1 B			0.63 C	0.83 B	1.09 A

[w] Applications on 23, 27 April; 7, 14, 22 May; 1, 11, 21 June; 6, 23 July (sulfur and tebuconazole + captan treatments); and 10 September (sulfur treatment).
[x] Values are the mean of four replications. Means within a column followed by the same letter are not significantly different ($P = 0.05$) according to Duncan's multiple range test.
[y] High rate applied on 27 April and 11 May; low rate on 22 May, 1, 11, 21 June, 6, 23 July, 10 August (fenarimol treatment), and 28 August (myclobutanil treatment).
[z] Treatment included as a standard to measure relative disease control, not included in residue study.

Table 2. Incidence of scab and sooty blotch and yield of apple trees sprayed with sulfur or sterol demethylation inhibitor fungicides in 1991

Fungicide (a.i./ha)	Primary scab on McIntosh (%)		Fruit scab at harvest (%)				Sooty blotch (%) on Golden Delicious	Fruit yields by cultivar (kg/cm² of trunk diameter)		
	Spurs 16 May	Terminals 10 June	McIntosh 28 August	Delicious 16 September	Golden Delicious 30 September	Mean	30 September	McIntosh	Delicious	Golden Delicious
Sulfur 17.9 kg[v]	1.5 c[w]	1.3 b	7.1 d	4.4 d	4.5 bc	5.3 d	16.0 bc	0.23 a	0.35 bc	0.25 a
Myclobutanil 140.2 g + sulfur 9.0 kg[x]	9.4 c	0.8 b	18.9 cb	39.0 c	5.5 bc	21.2 c	2.8 c	0.23 a	0.85 a	0.16 a
Myclobutanil 140.2 g[y]	4.5 c	0.8 b	20.1 c	38.1 c	3.8 c	20.7 c	14.5 bc	0.22 a	0.70 ab	0.29 a
Fenarimol 52.6 g + sulfur 9.0 kg[x]	60.2 b	2.6 b	53.5 b	74.5 b	17.2 b	48.4 b	0.6 c	0.09 a	0.31 bc	0.20 a
Fenarimol 78.8 g + sulfur 9.0 kg[y]	3.8 c	0.5 b	21.4 c	30.6 c	14.1 bc	22.0 c	2.8 c	0.15 a	0.60 ab	0.32 a
Fenarimol 78.8 g[x,z]	5.9 c	0.7 b	20.7 c	41.8 c	9.4 bc	23.9 c	40.3 ab	0.33 a	0.47 abc	0.21 a
Tebuconazole 189.2 g + captan 2.2 kg[x,z]	0.4 c	0.0 b	1.1 e	3.7 d	1.1 c	1.9 d	0.6 c	0.24 a	0.52 abc	0.24 a
Unsprayed control	98.4 a	66.7 a	100.0 a	98.2 a	98.2 a	98.8 a	60.9 a	0.00 a	0.16 c	0.11 a
Cultivar means			30.3 B	41.3 A	19.2 C			0.19 B	0.49 A	0.23 B

[v] Sulfur applied on 8, 11, 18, 29 April; 9, 19, 29 May; 13, 27 June; 11, 25 July; and 7, 21 August.
[w] Each value is the mean of four replications. Means within a column followed by the same letter are not significantly different ($P = 0.05$) according to Duncan's multiple range test.
[x] Applied alone (except tebuconazole + captan) on 11, 18 April and 2 May; then alone or mixed with sulfur (where indicated) on 9, 19, 29 May, 13, 27 June, and 11 July. Sulfur only was applied to the myclobutanil plot on 25 July and 7, 21 August; and fenarimol with sulfur was applied to the fenarimol + sulfur plot on 25 July and 5 August and sulfur only on 21 August; fenarimol alone and tebuconazole + captan were applied on 25 July.
[y] Myclobutanil applied alone from 11 April to 25 August as described in footnote above, plus a final spray on 21 August. Fenarimol + sulfur applied as described in footnote above except the third spray was on 30 April and the final spray on 5 August.
[z] Treatments included as standards for measuring relative disease control not included in residue study.

separatory funnel with 60 ml of 5% NaCl and 50 ml of methylene chloride. For juice, the sample was extracted with 3–25 ml portions of methylene chloride. The methylene chloride extracts were evaporated to dryness, and the residue was redissolved in hexane.

Sulfur residue was determined by blending 50 g of apple flesh, sauce, or frozen slices in 100 ml of acetone for 3 min and filtering the extract through a Whatman #1 filter in a Buchner funnel. Deionized water (35 ml) was added when blending concentrated juice. Extracts, along with 50 ml of acetone used to wash the funnel and residue, were partitioned by shaking for 2 min with 150 ml, then 50 ml, of methylene chloride. A 25-g juice sample was extracted with 3–20 ml portions of methylene chloride. The methyl chloride extracts were combined, percolated through a bed of anhydrous Na_2SO_4, which was washed with 20 ml of methylene chloride, and evaporated to dryness with a rotary vacuum at 30 C. Residues were redissolved in 25 ml of methylene chloride and filtered; and after a second methylene chloride treatment, the volume was reduced again to dryness and then made up to 1 ml with hexane.

Analyses for myclobutanil and fenarimol were carried out by using a gas chromatograph equipped with a ^{63}Ni electron capture detector and a 30 m × 0.323 mm inside-diameter capillary column (0.25 μm film thickness: J & W DB-5 column, ANSPEC Company, Ann Arbor, MI). The samples were run under the following conditions: column flow rate was 1 ml/min helium; makeup gas flow was 58 L/min nitrogen; anode purge was 4 ml/min nitrogen; column temperatures were 230 and 240 C for fenarimol and myclobutanil, respectively; detector temperature was 300 C; and injector temperature was 250 C.

Sulfur was analyzed by using a gas chromatograph equipped with a flame photometric detector in the sulfur mode and a 30 m × 0.53 mm inside-diameter J & W DB-5 (1.5 μm film thickness) megabore column. The samples were run under the following conditions: column flow rates were 10 L/min helium, 150 ml/min hydrogen, and 150 ml/min air; column, detector, and injector temperatures were 180, 275, and 250 C, respectively.

Fortification studies at the 0.01-ppm level for all sample types yielded an average 87, 91, and 101% recovery for myclobutanil, fenarimol, and sulfur, respectively.

Disease development and ratings. Apple scab infection periods were monitored with an electronic disease predictor (6) (Reuter-Stokes, Twinsburg, OH). The discharge of ascospores was monitored in the field with Rotorod Samplers (16) (Sampling Technologies, St. Paul, MN) controlled with an electronic wetness sensing unit (12). The incidence of scab on leaves of fruiting spurs and terminal shoots of McIntosh was evaluated by rating 20 spurs and terminals per replicate. Fruit scab was evaluated by examining one to two field crates of apples harvested from each tree in the experiment. Fruit of Golden Delicious were also examined for sooty blotch. The percentage of leaves and fruit infected were calculated and subjected to analysis of variance.

RESULTS

Apple scab control. In 1990, apple scab infection periods (and severity) were identified on 19 April (moderate), 4 May (low), 12 May (moderate), 14 May (high), 17 May (low), 19 May (moderate), 25 May (moderate), 2 June (low), and 8 June (low). Peak ascospore discharge occurred on 4 May, and the last discharge period was detected on 8 June. The first scab lesions were noted on 19 May.

When the data for the incidence of fruit scab in 1990 and in 1991 were analyzed by a split-plot analysis, *F* values for cultivar, treatment, and interaction effects were all highly significant (Table 3). Over all treatments, the incidence of fruit scab at harvest in 1990 was higher on McIntosh than on Delicious or Golden Delicious, and 96–100% of the fruit on unsprayed trees were infected (Table 1). Over all cultivars, the tebuconazole-captan mixture was the most effective treatment. Sulfur and myclobutanil treatments were similar in effectiveness, followed by the fenarimol treatments. Control of fruit scab was not improved where application rates of myclobutanil and fenarimol were increased in two sprays early in the season.

In 1991, apple scab infection periods (and severity) were detected on 8 April (high), 14 April (moderate), 19 April (low), 27 April (moderate), 5 May (moderate), 16 May (moderate), 24 May (moderate), 25 May (high), and 2 June (high). The first ascospores were trapped on 4 April, the most on 8 April, and the last on 30 May. The severity of primary apple scab was greater in 1991 than in 1990. The first scab lesions were observed on 28 April 1991 vs. 19 May 1990, and 98.4% of the spur leaves were scab infected on 16 May 1991 vs. 28.2% on 1 June 1990 (Tables 1 and 2).

Over all treatments, the incidence of fruit scab at harvest in 1991 was higher for Delicious than for McIntosh and Golden Delicious, and 98–100% of the fruit on unsprayed trees were infected (Table 2). Over all cultivars, the tebuconazole-captan treatment and the sulfur treatment were the most effective. Treatments of myclobutanil alone or mixed with sulfur were similar in effectiveness for reducing fruit scab to treatments of 78.8 g/ha of fenarimol alone or mixed with sulfur. The 52.6 g/ha of fenarimol plus sulfur mixture was the least effective spray treatment.

Sooty blotch control. The incidence of sooty blotch on fruit of Golden Delicious was moderate in 1990 and light in 1991 (Tables 1 and 2). In 1990, the incidence of sooty blotch on fruit from trees sprayed with myclobutanil or fenarimol was similar to the incidence on fruit from unsprayed trees. In 1990 but not in 1991, fruit from trees sprayed with sulfur had significantly ($P = 0.05$) less sooty blotch than fruit from trees sprayed with myclobutanil or fenarimol. For treatments which included a DMI fungicide, fruit from trees sprayed with myclobutanil or fenarimol mixed with sulfur in 1991, or with the tebuconazole–captan mixture in 1990 and 1991, had the lowest incidence of sooty blotch.

Fruit yields. When the yield data were subjected to a split-plot analysis, *F* values for cultivar were significant in 1990 and 1991, and the value for treatment was very significant in 1990 (Table 3). Yields of Golden Delicious trees were higher than yields of McIntosh and Delicious trees in 1990, and yields of Delicious trees were higher than yields of McIntosh and Golden Delicious in 1991 (Tables 1 and 2). Unsprayed trees of each cultivar yielded significantly less than most

Table 3. Analysis of variance for the incidence of apple scab and yield of apple trees treated with fungicide spray programs over 2 yr (1990–1991)

	Fruit scab (%)				Yield (kg/cm² of trunk diameter)			
	1990		1991		1990		1991	
Source	df	Mean squares	df	Mean squares	df	Mean squares	df	Mean squares
Replication	3	468.2	3	168.9	3	0.269	3	0.118
Treatment	6	12,819.1***[z]	7	11,548.0***	6	0.525***	7	0.143
Error a	18	128.4	21	113.2	18	0.079	21	0.071
Cultivar	2	4,775.9***	2	3,897.4***	2	1.475**	2	0.856**
Treatment × cultivar	12	555.4***	14	451.3***	12	0.110	14	0.064
Error b	48	82.2	48	56.9	42	0.057	48	0.070

[z] Three asterisks indicate that the *F* value was significant at $P < 0.001$, two asterisks at $P < 0.01$.

sprayed trees in 1990, but except for some treatments on Delicious, yields of unsprayed trees were not significantly different from yields on sprayed trees in 1991. There was no consistent difference in yields among the spray treatments.

Fungicide residues. Tolerance levels permitted in raw apple fruit by EPA are 0.5 ppm for myclobutanil and 0.1 ppm for fenarimol. Residue levels in processed products cannot exceed that for the raw fruit. Sulfur is excepted from tolerance.

Residues of 6.9–17.4 and 5.8–13.6 ppm of sulfur were detected on unwashed raw fruit in 1990 and 1991, respectively (Table 4). Residues of sulfur in apple slice, sauce, and juice samples from washed and peeled apples were less than 1.0 ppm.

In 1990, sprays of myclobutanil at 66 and 13 days before harvest of the cultivar McIntosh left residues on raw fruit of 8.8–13.1 and 62.9–75.2 ppb, respectively, or about 3 and 14% of the tolerance (Table 4). Residues in apple slices and sauce were similar and were about 2 and 6% of the tolerance for the 66- and 13-day intervals, respectively. Residues of myclobutanil in juice concentrate were increased slightly over apple slice and sauce samples but were still far below the tolerance. Single-strength juice had the lowest level of detectable residue. Sprays of fenarimol 66 and 31 days before harvest of McIntosh apples left residues on raw fruit of 2.4–5.3 and 7.5–18.8 ppb, respectively, or about 4 and 12% of the tolerance. Residues in apple slices and sauce were similar and about 1 and 3% of the tolerance for the 66- and 31-day intervals, respectively. Residues of fenarimol in juice concentrate

Table 4. The effect of applications of sulfur, myclobutanil, and fenarimol for disease control on residue accumulation in raw and processed apples in 1990 and 1991

Treatment (a.i./ha)	Sprays (no.)	Total (kg a.i./ha)	Cultivar (PHI days)[v]	Fungicide residues (ppb, sulfur in ppm)[w]				
							Apple juice	
				Raw fruit	Frozen apple slices	Apple sauce	Concentrate	Single strength
1990 Growing season								
Sulfur 22.4 kg	11	246.40	McIntosh (0)	17.4 a[x]	0.4	...[y]	nd[y]	nd
			Delicious (18)	12.0 ab	0.2	nd	nd	nd
			Golden Delicious (31)	6.9 b	0.4	nd	nd	nd
				$P = 0.01$[z]				
Myclobutanil 140.2 g	9	1.26	McIntosh (66)	13.1	11.3	...	24.3	3.5
			Delicious (84)	8.8	12.1	4.8	5.6	nd
			Golden Delicious (97)	11.9	7.0	6.7	5.5	4.4
				NS				
Myclobutanil 224.3/140.2 g	9	1.43	McIntosh (13)	68.0	19.7	...	32.0	6.9
			Delicious (31)	75.2	21.6	22.7	26.3	6.4
			Golden Delicious (44)	62.9	29.6	18.8	23.9	6.6
				NS				
Fenarimol 52.6 g	9	0.47	McIntosh (66)	3.0	0.6	0.5	0.2	nd
			Delicious (84)	2.4	nd	0.5	nd	nd
			Golden Delicious (97)	5.3	1.1	1.1	0.1	nd
				NS				
Fenarimol 105.2/52.6 g	9	0.58	McIntosh (31)	18.8	3.8	2.9	1.3	0.1
			Delicious (49)	8.0	4.1	2.6	0.1	nd
			Golden Delicious (62)	7.5	1.6	2.5	0.9	nd
				NS				
1991 Growing season								
Sulfur 17.9 kg	13	232.70	McIntosh (7)	13.6 a	0.7	0.1	nd	nd
			Delicious (26)	5.2 b	0.1	0.1	nd	nd
			Golden Delicious (40)	5.8 b	0.9	nd	nd	nd
				$P = 0.05$				
Sulfur 9.0 kg	9	81.00	McIntosh (7)	12.2 a	0.8	0.1	nd	nd
			Delicious (26)	1.9 b	0.8	0.8	nd	nd
			Golden Delicious (40)	3.0 b	nd	nd	nd	nd
				$P = 0.003$				
Myclobutanil 140.2 g	9	1.26	McIntosh (48)	28.1	15.9	11.2	10.2	1.9
			Delicious (67)	32.0	5.4	8.0	5.9	2.0
			Golden Delicious (81)	24.0	8.6	8.6	3..9	2.3
				NS				
Myclobutanil 140.2 g	11	1.63	McIntosh (7)	107.2 a	21.8	15.8	28.9	6.1
			Delicious (26)	75.1 b	12.4	15.8	16.3	4.8
			Golden Delicious (40)	90.7 ab	26.6	19.1	18.5	4.0
				$P = 0.03$				
Fenarimol 52.6 g	11	0.58	McIntosh (23)	23.3	7.9	6.7	4.4	0.8
			Delicious (42)	12.2	4.9	5.4	1.8	0.5
			Golden Delicious (56)	14.4	2.2	5.0	3.9	1.0
				NS				
Fenarimol 78.9 g	11	0.87	McIntosh (23)	28.1	12.1	8.2	4.5	2.0
			Delicious (42)	17.3	3.6	5.7	2.8	0.7
			Golden Delicious (56)	15.4	6.8	7.6	2.8	1.2
				NS				

[v] PHI = preharvest spray interval in days from last application to harvest.

[w] EPA tolerance levels: myclobutanil = 0.5 ppm, fenarimol = 0.1 ppm, sulfur = exempt from tolerance. Detection limits: myclobutanil = 1.5 ppb, fenarimol = 0.33 ppb, sulfur = 0.04 ppm.

[x] Values are means of nine raw fruit (three each for replicates 1–3; fruit from replicate 4 were held as backup samples) and of two subsamples for slice, sauce, and juice samples. Means in raw fruit column followed by the same letter do not differ at $P < 0.05$ according to Duncan's multiple range test.

[y] ... = No samples; nd = not detected.

[z] Significance ($P > F$) of analysis of variance model; NS = not significant at $P = 0.05$.

were not increased over slice and sauce samples, and except for one sample, were not detected in single-strength juice.

In 1991, sprays of myclobutanil at 48 and 7 days before harvest of McIntosh apples left residues on raw fruit of 18.1–32.0 and 75.1–107.2 ppb, respectively, or about 5 and 19% of the tolerance (Table 4). Residues in apple slices and sauce were similar and about 2 and 4% of the tolerance for the 48- and 7-day intervals, respectively. Residues of myclobutanil in juice concentrate were similar to those in apple slice and sauce samples and far below the tolerance. Single-strength juice had the lowest level of detectable residue, only 1% of the tolerance.

Spray programs with a total for the season of 578.6 and 867.9 g/ha of fenarimol left residues on raw fruit of 12.2–23.3 and 15.4–28.1 ppb, respectively, or about 17 and 21% of the tolerance level (Table 4). Residues in apple slices and sauce were 6–8% of the tolerance. Residues of fenarimol in juice concentrate were not increased over apple slice and sauce samples. Single strength juice had residues approximately 1% of the tolerance.

The spray interval between last application and harvest suggested by EPA to avoid excessive spray residues on apples is 14 days for myclobutanil and 30 days for fenarimol. At these preharvest intervals (PHIs), residue levels were well below the residue tolerance established by EPA. Residues on fruit from treatments with shorter PHIs (7 and 23 days in 1991 for myclobutanil and fenarimol, respectively) were well below established tolerances (Table 4). Residue levels were also very low for treatments of myclobutanil and fenarimol with PHIs of 97 and 97 days in 1990 and of 81 and 56 days in 1991, respectively.

DISCUSSION

The programs evaluated in this study relied on fenarimol, myclobutanil, and sulfur because EPA has classified many alternative fungicides as possible or probable carcinogens (1,2). If the EPA adheres to the Delaney clause, registrations of many fungicides currently used on apples will be canceled, and apple growers will be forced to rely heavily on the fungicides included in this study for disease control. Apple scab programs that rely on fenarimol or myclobutanil have several limitations. As demonstrated in this study and in efficacy studies conducted in other states (14,15), neither fungicide controls sooty blotch. Furthermore, fruit quality may be reduced due to increased fruit scab in orchards with high levels of scab inoculum. By adopting fungicide programs that utilize only sterol demethylation inhibitor (DMI) fungicides, there is risk of a shift in the population of *V. inaequalis* to strains with reduced sensitivity or resistance (5,7,13).

Processed apple products were included in this study because of potential concerns that residues would increase, particularly in the juice concentrate. Myclobutanil and fenarimol were selected in part because these heat-stable, systemic fungicides were likely to remain after processing. Residues of myclobutanil in raw and processed products were higher than those of fenarimol because more myclobutanil than fenarimol was applied per hectare and possibly because of differences in uptake or metabolism of the respective fungicides. Although concentrations of myclobutanil but not of fenarimol were often slightly higher in juice concentrate than in slices or sauce, pesticide residues did not routinely undergo a 10-fold concentration when processed into juice concentrate. Because of the sensitive techniques we used to detect DMI fungicides, our studies revealed that apples treated with nine to 11 applications of myclobutanil or fenarimol are likely to contain low residues at harvest. Our study represents a worst-case situation because growers use DMI fungicides to control early-season diseases, then switch to different fungicides because DMI fungicides are not effective against summer diseases such as sooty blotch.

Tank mixing a contact fungicide with the DMI fungicide could overcome problems of suboptimum control of fruit scab and of pathogens not controlled by DMI fungicides. Under the severe conditions for disease in the test orchard, the tebuconazole–captan mixture gave excellent control of scab and sooty blotch. The contact fungicides captan, benomyl, mancozeb, metiram, and maneb are often tank mixed with DMI fungicides to increase the disease control spectrum and to improve control of fruit scab. However, EPA considers that all of these contact fungicides have potential oncogenic risk (1,2). In 1990, the control of fruit scab was not improved when 9 kg/ha of sulfur was tank mixed with myclobutanil or fenarimol. In regions where sooty blotch is more severe than in Michigan, sulfur has not provided adequate control of this disease (15), while mancozeb, captan, and benomyl were effective (3,14). Although processed products made from washed and peeled apples contained no detectable sulfur, the mediocre efficacy of sulfur will limit its use in tank mixes with DMI fungicides.

Since the fungicides of concern to EPA are largely contact fungicides, it may be possible to develop methods, such as washing or temperature treatments, to remove residues. In our study, sulfur was at or below the limit of detection in apple products made from washed and peeled apples. Such methods may be needed, because the strategy of increasing the interval between last application and harvest to reduce residues risks late-season outbreaks of diseases such as sooty blotch.

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