Reduction of Azinphos-methyl, Chlorpyrifos, Esfenvalerate, and Methomyl Residues in Processed Apples

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McIntosh, Red Delicious, and Golden Delicious from two years of experimental spray programs using azinphos-methyl, chlorpyrifos, esfenvalerate, and methomyl were processed into frozen apple slices, applesauce, single-strength juice, and juice concentrate. Residue levels were expressed as micrograms per 150 g of apple or the equivalent amount of apple product to calculate the percentage change in these pesticides brought about by processing. Producing single-strength apple juice reduced azinphos-methyl, chlorpyrifos, esfenvalerate, and methomyl residues by 97.6, 100, 97.8, and 78.1%, respectively. Production of applesauce reduced all four compounds by ≥95%. Azinphos-methyl, chlorpyrifos, esfenvalerate, and methomyl residues were reduced in apple slices by 94.1, 85.7, 98.6, and 94.7%, respectively. Processing is shown to be very effective in reducing the levels of these pesticides.

Keywords: *Pesticides; azinphos-methyl; chlorpyrifos; esfenvalerate; methomyl; apples; food processing; apple slices; applesauce; apple juice*

INTRODUCTION

As part of a study of the potential for zero residue disease control programs for Michigan apples, four pesticides were included in the spray program. The efficacy of disease control and fungicide residues in raw and processed apples of three cultivars of apple (*Malus* × *domestica*) on scab and sooty blotch has been published previously (Jones et al., 1993).

Concerns expressed about residues in processed foods frequently reflect a lack of knowledge about food-processing operations and their effect on residue levels. Processing has been interpreted as any operation performed on a food, food source, or food product from the point of harvest through consumption (Ritchey, 1981). Unit operations in processing typically include washing the raw product with large volumes of water, frequently using high-pressure sprays and often incorporating surfactants or other washing aids; peeling the product mechanically with knives, abrasive disks, or water; blanching with hot water or steam; and, in the case of canned or cooked foods, the cooking of the product at temperatures at or above the boiling temperature of water. Thus, the residues that may be present are subject to not only physical removal by washing or peeling but also acid or base hydrolysis and thermal degradation (Chin, 1991).

The consensus among those familiar with food-processing methods is that pesticide residues decrease, often dramatically, during processing and food preparation (Chin, 1991; Ritchey, 1981; Zabik, 1987). Publication of the effect of processing on residue levels of four pesticides included in this study provides data to alleviate recent concern for the level of pesticide residues in foods, particularly those foods eaten by children. The two year study used McIntosh, Red Delicious, and Golden Delicious apples that were analyzed fresh and after processing into slices, applesauce, and juice. The four pesticides used were azinphos-methyl [*O*,*O*-dimethyl-*S*-[(4-oxo-1,2,3-benzotriazine-3(4*H*)-yl) methyl] phosphorodithioate], chlorpyrifos [*O*,*O*-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate], esfenvalerate [(*S*)-cyano(3-phenoxyphenyl)methyl (*S*)-4-chloro-α-(1-methylethyl)benzeneacetate], and methomyl [*S*-methyl-*N*-[(methylcarbarbamoyl)oxy]thioacetamidate].

MATERIALS AND METHODS

Orchard Applications. Jones et al. (1993) described the orchard layout and spray programs. In 1990, treatment I included esfenvalerate, Asana XL 0.66 applied at 10 g of active ingredient (ai)/acre, which was applied four times between April 27 and August 21. Treatments II and V used azinphos-methyl, Guthion 35, applied at 476 g of ai/acre, which was applied four times between April 27 and September 4. Treatments III and IV included chlorpyrifos, Lorsban 50W, applied four times at 340 g of ai/acre for the first spray on April 27 and the last spray on August 13 and at 680 g of ai/acre for the middle two sprays as well as methomyl, Lannate 90SC, which was applied once on April 27 at the rate of 408 g of ai/acre. McIntosh apples were harvested on September 10, Red Delicious on September 28, and Golden Delicious on October 11 in 1990. For 1991, treatments I and II used esfenvalerate, Asana XL 8.4% EC, applied at 10 g of ai/acre, six times from April 29 to August 14 for treatment I and from May 2 to August 7 for treatment II. Treatment III included chlorpyrifos, Lorsban 50W, applied at 340 g of ai/acre, six times from May 2 to August 7, and methomyl, Lannate 90SC, applied at 408 g of ai/acre, four times between May 2 and July 11. Treatment IV had five applications of chlorpyrifos applied from May 2 to July 25, and four applications of methomyl applied from May 2 to July 11. Treatment V had azinphos-methyl, Guthion 35W, applied at 476 g of ai/acre five times between April 30 and

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July 25. McIntosh apples were harvested on August 28, Red Delicious on September 16, and Golden Delicious on September 30 in 1991.

Sampling and Harvesting Fruit. At the time of optimum maturity for each cultivar, 18 fruit for the raw fruit residue analyses were collected from a height of 1.5−2.0 m above the ground and from the inside and outside regions of each tree. The remaining fruit on each tree were harvested into labeled field crates. Only the fruit of the Golden Delicious were hand thinned in late July 1990. Fruit from all other cultivars in 1990 and all cultivars in 1991 were not hand 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, applesauce, and juice. Apples not processed on the day of harvest were held at 3 °C prior to processing and were always processed within 3 days. Fruit were washed in cold, flowing tap water for 5 min and 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, and 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 at −20 °C immediately. Slices for sauce were placed on stainless steel trays and steamed for 6−9 min so that the slice temperature reached 96−99 °C for 3−4 min. The cooked slices were discharged into a Langsencamp pulper with a 1.5 mm screen operating at ∼1000 rpm. The hot applesauce 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 month later, portions of each frozen juice sample were removed from the freezer, thawed, and concentrated under vacuum to 70−72 °Brix (∼7-fold concentration). After each sample was processed, the processing equipment was thoroughly cleaned to avoid cross-contamination of samples with residues.

Analytical Procedures. Pesticide residues on the fruit surface were determined for methomyl from the water wash and for the remaining pesticides from the dichloromethane wash. Apples from each replicate were stabbed through the core with a stainless steel skewer and immersed in a known volume of water followed by dichloromethane. Apples were spun continuously for 3 min for the water wash and for 2 min for the dichloromethane wash. After the fruit was washed, all of the fruit for each replication (9−10 apples) were chopped in a Hobart food chopper and thoroughly mixed to ensure homogeneity. Frozen apple slices were also chopped. Applesauce and juice were used directly after the product thawed. Chlorpyrifos and azinphos-methyl residues were extracted and cleaned up using the method described in the *Pesticide Analytical Manual* (U.S. Food and Drug Administration, 1990) for chlorpyrifos in peaches. Methomyl was extracted as outlined by Pease and Kirkland (1968) and adapted by Fung (1975). This procedure was based on a gas chromatographic measurement of methomyl and methomyl oxime after subsequent alkaline hydrolysis. Both compounds were quantitated, and the results were back-calculated to give a total methomyl residue. Esfenvalerate residues were extracted and cleaned up according to the method described in a technical report of Shell Development Co. (1986).

Residues of azinphos-methyl, chlorpyrifos, methomyl, and methomyl oxime were determined using a Beckman GC-65 gas chromatograph equipped with a flame photometric detector (FPD) and a fused silica capillary column (15 m megabore × 0.53 mm i.d.) coated with 1.5 μm DB-1 film. Chlorpyrifos and azinphos-methyl were detected with the FPD in the phosphorus mode, whereas methomyl and methomyl oxime were detected in the sulfur mode. The gas chromatograph was operated isothermally in the direct injection mode and employed the following conditions: for chlorpyrifos, column, inlet, and detector temperatures were 235, 250, and 285 °C, respectively, with a nitrogen flow rate of 18 mL/min and a 30 psi head pressure and with hydrogen and air flow rates of 175 and 179 mL/min, respectively; for azinphos-methyl, column, inlet, and detector temperatures were 265, 270, and 285 °C, respectively, with a nitrogen flow rate of 27 mL/min and a 42 psi head pressure and with hydrogen and air flow rates of 150 and 170 mL/min, respectively; for methomyl, the temperatures were 200, 280, and 285 °C for column, inlet, and detector, respectively, with gas flow rates of 30, 150, and 170 mL/min for nitrogen, hyrogen, and air, respectively; finally, the temperatures for methomyl oxine were 140, 250, and 285 °C for column, inlet, and detector temperatures, respectively, and gas flow rates were 5, 150, and 170 mL/min, respectively. Esfenvalerate residues were measured by a Perkin-Elmer GC 8500, equipped with ^{63}Ni electron capture detector (ECD), using a 30 m × 0.32 mm i.d. fused silica capillary column and coated with a 25 μm DB-5 film. The oven temperature was isothermal at 270 °C, the injector temperature was 290 °C, and the detector temperature was 340 °C. The carrier gas was helium at 1 mL/min and the makeup gas nitrogen at 30 mL/min. Esfenalerate elutes as two discrete peaks under the GC conditions used in this method. Therefore, both peaks were considered in the calculation.

All solvents were of pesticide grade. Analytical standards of azinphos-methyl, chlorpyrifos, methomyl, and methomyl oxime were obtained from the U.S. Environmental Protection Agency, Pesticide and Industrial Chemical Repository, Research Triangle Park, NC. Esfenvalerate was obtained from E. I. DuPont de Nemours & Co. Inc., Wilmington, DE. Average recovery percentages using the above methods were 93.5, 73.4, 60.6, and 76.6% for esfenvalerate, azinphos-methyl, chlorpyrifos, and methomyl, respectively.

RESULTS AND DISCUSSION

The levels of esfenvalerate, chlorpyrifos, azinphos-methyl, and methomyl, expressed as nanograms per gram of the whole apple, apple slices, applesauce, juice concentrate, and single-strength juice, are presented in Table 1 for 1990 data and in Table 2 for 1991 data. Values for the fresh fruit include the residues on the surface of the apple from the water and dichloromethane washes as well as the residues in the remaining apple (El-Hadidi, 1993). The residue levels expressed as parts per billion in Tables 1 and 2 show a substantial reduction in these pesticide residues in the processed apple products. Expressing residue values as nanograms per gram does not allow for a true comparison as some of the original material is lost during the various processing steps so that raw and processed weights are not equivalent. Therefore, to calculate the true percentage reduction, the nanograms per gram value of residue must be converted into micrograms in the fresh apple and in the processed apple products. Using product yield data for apple products prepared according to the same processing methods and from the same apple cultivars harvested from the same experimental plot at Michigan State University, micrograms of pesticide residue in fresh and processed apple products were calculated and are presented in Table 1 for 1990 data and in Table 2 for 1991. Average product yield data from 1993, 1994, and 1995 for apple slices was 73%, for applesauce, 27%, and for single-strength juice, 584.7 mL/kg (Siler, 1998). Because apple juice concentrate was prepared by evaporating single-strength juice to a range of degrees Brix, no yield data were available. Single-strength concentration of juice represents the juice as consumed. From these data, the percentages of esfenvalerate, chlorpyrifos, azinphos-methyl, and methomyl residues lost during processing were calculated and are presented in Table 3.

Methomyl, which was used early in the spray programs in 1990, was not found in the fresh fruit or

Table 1. Insecticide Residues on and in Apple Fresh Fruits and Fruit Products at the Optimum Harvest Time [Nanograms per Gram and Total Micrograms—1990 Data]

insecticide spray treatment	apple cultivar	preharvest intervals, days	insecticide residues: whole fruits ng/g	whole fruits μg	slices ng/g	slices μg	sauce ng/g	sauce μg	juice, concentate ng/g	juice, single ng/g	juice, single μg
esfenvalerate (I)	McIntosh	20	67.1	10.07	1.9	0.21	–[a]	–	ND[b]	ND	ND
	Red Delicious	38									
	Golden Delicious	51									
minimum detection limits			0.4	0.06[c]	0.4	0.04[c]	0.4	0.01[c]	0.4	0.4	0.04[c]
chlorpyrifos (III)	McIntosh	28	19.4	2.91	8.8	0.96	–	–	7.2	ND	ND
	Red Delicious	46	11.6	1.74	3.5	0.38	ND	ND	7.8	ND	ND
	Golden Delicious	59	23.6	3.54	8.8	0.96	ND	ND	4.6	ND	ND
chlorpyrifos (IV)	McIntosh	28	29.9	4.49	9.7	1.06	2.4	0.10	7.0	ND	ND
	Red Delicious	46	17.1	2.57	6.0	0.66	ND	ND	6.9	ND	ND
	Golden Delicious	59	51.1	7.67	10.7	1.17	3.1	0.13	3.7	ND	ND
minimum detection limits			0.4	0.06[c]	0.4	0.04[c]	0.4	0.01[c]	0.4	0.4	0.04[c]
azinphos-methyl (II)	McIntosh	6	313.6	47.04	24.6	2.69	–	–	129.2	23.0	2.02
	Red Delicious	24	242.6	36.39	11.6	1.27	ND	ND	63.4	5.1	0.45
	Golden Delicious	37	68.7	10.31	7.0	0.77	5.3	0.21	28.7	ND	ND
azinphos-methyl (V)	McIntosh	6	340.0	51.00	57.5	6.30	24.8	1.00	45.7	15.7	1.38
	Red Delicious	24	158.0	23.70	15.5	1.70	ND	ND	82.9	8.3	0.45
	Golden Delicious	37	108.6	16.29	ND	ND	ND	ND	22.2	ND	ND
minimum detection limits			4.0	0.60[c]	4.0	0.43[c]	4.0	0.14[c]	4.0	4.0	0.15[c]
methomyl (III, IV)	McIntosh	137	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Red Delicious	155	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Golden Delicious	168	ND	ND	ND	ND	ND	ND	ND	ND	ND
minimum detection limits			1.5	0.23[c]	5.0	0.54[c]	5.0	0.18[c]	5.0	5.0	0.44[c]

[a] Missing during processing. [b] Not detectable. [c] μg/150 g of apple or equivalent amount of processed apple product.

Table 2. Insecticide Residues on and in Apple Fresh Fruits and Fruit Products at the Optimum Harvest Time [Nanograms per Gram and Total Micrograms—1991 Data]

insecticide spray treatment	apple cultivar	preharvest intervals, days	insecticide residues: whole fruits ng/g	whole fruits μg	slices ng/g	slices μg	sauce ng/g	sauce μg	juice, concentrate ng/g	juice, single ng/g	juice, single μg
	McIntosh	14	80.3	12.05	2.4	0.26	4.1	0.17	ND[a]	ND	ND
esfenvalerate (I)	Red Delicious	33	52.5	7.88	0.4	0.04	4.2	0.17	ND	ND	ND
	Golden Delicious	47	45.3	6.80	1.2	0.13	2.7	0.11	ND	ND	ND
esfenvalerate (II)	McIntosh	21	70.1	10.52	1.2	0.13	1.4	0.06	ND	ND	ND
	Red Delicious	40	38.9	5.84	0.4	0.04	3.3	0.13	ND	ND	ND
	Golden Delicious	54	34.7	5.21	ND	ND	2.3	0.09	ND	ND	ND
minimum detection limits			0.4	0.06[b]	0.4	0.04[b]	0.4	0.01[b]	0.4	0.4	0.04[b]
chlorpyrifos (III)	McIntosh	21	34.6	5.19	3.2	0.35	1.2	0.05	ND	ND	ND
	Red Delicious	40	18.1	2.72	ND	ND	ND	ND	ND	ND	ND
	Golden Delicious	54	48.3	7.25	0.9	0.01	ND	ND	ND	ND	ND
chlorpyrifos (IV)	McIntosh	34	10.3	1.54	0.6	0.07	0.9	0.04	ND	ND	ND
	Red Delicious	53	9.7	1.45	ND	ND	ND	ND	ND	ND	ND
	Golden Delicious	67	16.9	2.53	ND	ND	ND	ND	ND	ND	ND
minimum detection limits			0.4	0.06[b]	0.4	0.04[b]	0.4	0.01[b]	0.4	0.4	0.04[b]
azinphos-methyl (V)	McIntosh	34	174.1	26.12	57.5	6.30	6.8	0.28	94.6	29.5	2.59
	Red Delicious	53	78.0	11.70	15.5	1.70	ND	ND	22.2	13.2	1.16
	Golden Delicious	67	28.9	4.34	ND	ND	ND	ND	ND	ND	ND
minimum detection limits			4.0	0.06[b]	4.0	0.43[b]	4.0	0.14[b]	4.0	4.0	0.15[b]
methomyl (III)	McIntosh	48	46.6	6.99	10.2	1.12	10.2	0.41	ND	13.3	1.17
	Red Delicious	67	12.8	1.92	ND	ND	ND	ND	ND	10.7	0.94
	Golden Delicious	81	<5.0	<0.75	ND	ND	ND	ND	ND	ND	ND
minimum detection limits			5.0	0.75	5.0	0.54[b]	5.0	0.54[b]	5.0	5.0	0.44[b]

[a] Not detectable. [b] μg/150 g of apple or equivalent amountof processed apple product.

processed apple products. Levels of methomyl residues in 1991 were reduced by ~84% in all McIntosh apple products and were completely eliminated in apple slices and applesauce made from Red Delicious or Golden Delicious apples. Juice from Red Delicious apples harvested in 1991 showed a 51% reduction. These data appear to be an anomaly as the juice concentrate contained a nondetectable level of methomyl (Table 2).

Juice and applesauce had the greatest pesticide reduction, although all percentage reductions were high. For single-strength juice, there were average reductions of 97.8% of esfenvalerate, 100% of chlorpyrifos, and 97.6% of the azinphos-methyl residues. For applesauce, there were average reductions of 98.5% of esfenvalerate, 99% of chlorpyrifos, and 99.4% of azinphos-methyl residues. Juice was processed from macerated whole apples, whereas the applesauce was prepared by heating apple slices from peeled and cored apples.

Apple slices, which had been subjected to less processing than the applesauce in that the slices were not

Table 3. Percentage Reduction of Pesticides in Frozen Apple Slices, Applesauce, and Apple Juice Prepared from McIntosh, Red Delicious, and Golden Delicious Cultivars

insecticide spray treatment	year	apple cultivar	% reduction of insecticides: slices	sauce	juice (single)
esfenvalerate (I)	1990	McIntosh	97.9	–[a]	100
		Red Delicious	97.8	99.1	100
		Golden Delicious	100	98.7	100
esfenvalerate (I)	1991	McIntosh	97.8	98.6	90.0
		Red Delicious	99.5	97.8	90.1
		Golden Delicious	98.0	98.4	100
esfenvalerate(II)	1991	McIntosh	98.8	99.6	100
		Red Delicious	99.3	97.6	100
		Golden Delicious	100	98.3	100
chlorpyrifos (III)	1990	McIntosh	67.0	–	100
		Red Delicious	78.2	100	100
		Golden Delicious	72.8	100	100
chlorpyrifos (IV)	1990	McIntosh	76.4	97.7	100
		Red Delicious	74.3	100	100
		Golden Delicious	84.7	98.3	100
chlorpyrifos (III)	1991	McIntosh	93.3	98.7	100
		Red Delicious	100	100	100
		Golden Delicious	99.8	100	100
chlorpyrifos (IV)	1991	McIntosh	95.5	96.0	100
		Red Delicious	100	100	100
		Golden Delicious	100	100	100
azinphos-methyl (II)	1990	McIntosh	94.3	–	95.7
		Red Delicious	96.5	100	98.8
		Golden Delicious	92.5	98.1	100
azinphos-methyl (V)	1990	McIntosh	87.6	98.0	97.3
		Red Delicious	92.8	100	98.1
		Golden Delicious	100	100	100
azinphos-methyl (V)	1991	McIntosh	97.6	98.9	90.0
		Red Delicious	85.5	100	100
		Golden Delicious	100	100	100
methomyl (IV)	1991	McIntosh	84.0	94.1	83.3
		Red Delicious	100	100	51.0
		Golden Delicious	100	100	100

[a] Missing during processing.

heated, had slightly lower reductions of these pesticide residues. Apple slices had esfenvaterate residues reduced by an average of 98.8%, chlorpyrifos residues reduced by an average of 86.8%, and azinphos-methyl residues reduced by an average of 94.1%. The reduction of chlorpyrifos ranged from 67 to 85% in 1990 as compared to 93–100% in 1991. The reduction of esfenvalerate and azinphos-methyl residues in the frozen apple slices was more consistent for both years.

These data confirmed the findings of Ong et al. (1996), who prepared applesauce from washed and unwashed apples treated with azinphos-methyl. About 96% of azinphos-methyl was removed when applesauce was prepared from unwashed apples. The percentage of removal increased to 98% when the apples were washed before the applesauce was prepared.

Earlier studies of the effects of commercial and home preparation on pesticide residues in fruits and vegetables were summarized by Zabik (1987). These early studies showed residue reductions to be substantial, with percentage reductions of chlorinated hydrocarbons ranking from 50 to 99+% for commercial preparation and from 14 to 99+% for home preparation. With the exception of parathion in spinach and broccoli, commercial and home preparation substantially reduced organophosphate residues, with the reduction generally being in the high 80 or 90% range. Carbamate residues were reduced by 58–99+% when the vegetables were commercially processed but only by 11–92% in home preparation.

Elkins et al. (1972) studied the effect of heat processing and storage on pesticides in spinach and apricots. Five organophosphorus pesticides were included in the study: diazinon, azinphos-methyl, malathion, methyl parathion, and carbophenothion. Spinach was processed for 66 min at 252 °F, and apricots were processed for 50 min at 217 °F. Processing spinach reduced the compounds as follows: diazinon, 58%; azinphos-methyl, 100%; malathion, 96%; methyl parathion, 100%; and carbophenothion, 17%. At the end of storage for one year at ambient temperature these values were 100, 100, 99+, 100, and 71%, respectively. For apricots, processing reduced the organophosphate residues as follows: diazinon, 100%; azinphos-methyl, 61%; malathion, 32%; methyl parathion, 54%; and carbophenothion, 35%. At the end of storage for one year at ambient temperature these values were 100, 100, 84, 100, and 84%, respectively.

A recent study in Korea supports these earlier studies (Lee and Lee, 1997). These authors found that 45% of the organophosphate residues were eliminated when the foods were washed in water, 56% with detergent washing, 91% with peeling, 51% with blanching/boiling, and 90% in milling and processing.

Food processing substantially lowers the residues of pesticides in foods. The percentage reductions in the current study are supported by both early and more recent publications. These reductions are extremely important in evaluating the risk associated with ingestion of pesticide residues, especially for food products such as apples, which are eaten by young children. Fortunately, the reductions of residues during food processing enhance the safety of the food supply.

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