The Connecticut Agricultural Experiment Station, New Haven

Pesticide Residues in Produce Sold in Connecticut 1996

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A cooperative study by The Connecticut Agricultural Experiment Station and the Food Division of the Connecticut Department of Consumer Protection

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The Environmental Protection Agency (EPA) registers pesticides for use in the United States and sets tolerances for the amounts that remain in or on the produce after harvest (Code of Federal Regulations, 1996). Regulatory agencies, such as the U.S. Food and Drug Administration (FDA), and state agencies, such as the Connecticut Department of Consumer Protection, have the responsibilities to enforce the tolerances. In order to accomplish this, these agencies must know if a crop contains any pesticide residues, if the amount of these residues exceeds the allowable tolerance, or if a pesticide is present on a crop where it is not allowed. Effective action is also complicated since many crops are being sold at the same time they are in the laboratory for testing.

Pesticides are used on agricultural crops to control plant pests such as fungi, insects, and weeds. The use of these chemicals on the food supply is a major consumer safety issue. Furthermore, the ever-changing array of agrochemicals presents a challenge to the testing laboratory which has no knowledge of the actual chemicals used on a crop at the time of sampling, and hence must continually update its testing methods to detect new compounds and achieve lower detection levels of all analytes. For these reasons, the market basket study conducted by the Connecticut Department of Consumer Protection, in cooperation with the Department of Analytical Chemistry of The Connecticut Agricultural Experiment Station, remains part of an effective food safety program which assures consumers that produce grown in this state, other states, and foreign countries meets EPA pesticide tolerance levels.

This report presents the results of our 1996 market basket study on pesticide residues found in produce sold in Connecticut.

METHODS

Our market basket study starts with the collection of fresh and processed fruit and vegetable products. The samples are all collected at various Connecticut retailers and wholesale outlets by inspectors from the Connecticut Department of Consumer Protection, and are delivered to our laboratory in New Haven within 24 hours of collection. We refer to these market basket commodities as *surveillance* samples, since we have no prior knowledge of any pesticide use or misuse. When additional samples are obtained as a follow-up to a surveillance sample, they are referred to as *compliance* samples.

All samples are tested for pesticides using a multi-residue method developed in our laboratories (Pylypiw, 1993). Most fresh produce samples, such as apples, potatoes, spinach, beets, and snap-beans, are prepared as received, in their unwashed and unpeeled state. With other fresh samples, like cherries, bananas, peaches, and cantaloupe, only the edible portion is tested. Processed foods are prepared as received, although some procedures such as washing, chopping, mixing, or cooking most likely have been conducted. A weighed portion of each sample is blended with organic solvents to extract the pesticides from the sample. This extract is eventually injected into gas chromatographs with various detectors to determine how much, if any, pesticides are present. Our method is capable of determining pesticides with recoveries ranging from 81% to 114%, and has an average detection limit of 10 parts-per-billion.

Four years ago, we initiated the use of gas chromatography with a mass selective detector (GC-MSD) to confirm all violative residues. During the past 3 years, we expanded the use of GC-MSD for a large number of randomly selected samples (Pylypiw et al., 1994, 1995, 1996). Mass spectrometry identifies each pesticide by its unique fingerprint fragmentation pattern. The use of GC-MSD has allowed us to detect residues that did not respond to our other gas chromatograph detectors. For example, in 1995 this technique enabled us to identify and confirm the violative presence of the bird repellent, methiocarb, on blueberries from six different orchards. GC-MSD has also confirmed the presence of various older organochlorine pesticides such as chlordane and dieldrin in a variety of root and vine crops.

RESULTS AND DISCUSSION

In 1996 a total of 327 samples, representing a variety of fresh and processed foods, were tested. Of those 327 samples, 281 (85.9%) were fresh produce, and 46 (14.1%) were processed foods. Pesticide residues were found in 136 samples of fresh produce and two samples of processed products. The sample commodities and concentration ranges of all residues found in surveillance samples are given in Table 1 for fresh produce and Table 2 for processed foods. In response to these surveillance findings, 15 compliance samples were obtained to confirm the presence of violative pesticide residues. Results of all tests are forwarded to the Connecticut Department of Consumer Protection for regulatory enforcement.

None of the samples tested exceeded EPA tolerances, but four samples contained residues for which no EPA tolerance exists for that commodity. Specifically, one sample of snap-beans and one sample of winter squash contained 0.2 ppm and 0.022 ppm of the fungicide vinclozolin, respectively; one sample of endive contained 0.5 ppm of the insecticide chlorpyrifos; and one sample of pears contained 0.04 ppm of the fungicide iprodione. Twenty-four (8.5%) of the fresh produce samples were labeled as "organically grown." When tested, one sample of summer squash contained a detectable residue of endosulfan (Table 1). The residue was within the EPA tolerance for squash. However, Connecticut Organic Law states that any produce labeled as "organically grown" cannot contain any detectable pesticide residues (State of Connecticut, General Statutes).

Figure 1 shows all pesticides that were found and their frequency of occurrence in fresh produce samples from 1992 to 1996. Of particular interest are the pesticides that are most often found in our survey. Overall, the insecticide endosulfan is the most frequently detected residue. This is followed by the fungicides captan, iprodione, vinclozolin, and chlorothalonil. These fungicides are commonly found on fruits, including strawberries, apples, and peaches. This year, three additional pesticides were found and their presence in samples confirmed by GC-MSD. Specifically, these were the insecticide methoxychlor, and the fungicides folpet and ortho-phenylphenol. There was also a slight increase in the frequency of occurrence of chlordane and DDE, for reasons that will be discussed below.

PERSISTENT ORGANOCHLORINATED PESTICIDES

Twenty-two samples of fresh produce and one sample of processed food contained trace amounts of DDE (a soil metabolite of DDT), dieldrin, and/or chlordane (Tables 1 and 2). Specifically these were, one sample each of beets, beet tops, cabbage, collards, potatoes, and frozen spinach, two of eggplant and winter squash, four of cucumbers and lettuce, and seven of summer squash. In the United States the agricultural use of these organochlorine pesticides was banned in 1972; however, trace amounts have persisted in the environment (Pylypiw et al., 1991). Even though there is no EPA tolerance for these pesticides, the Food and Drug Administration (FDA) recognizes their persistence in the environment and has set action levels (allowable amounts) for these compounds in produce (Compliance Policy Guides, 1986). One sample of summer squash contained 0.12 ppm chlordane, which was above the 0.1 ppm FDA action level set for chlordane in squash.

These findings prompted us to examine our residue data from previous years. Although persistent organochlorine (POC) insecticides such as benzene hexachloride, dieldrin, DDT, chlordane, heptachlor, aldrin, and endrin have not been in common use on crops for over 25 years, trace residues of these compounds or their metabolites (DDE, heptachlor epoxide, etc.) have been detected by us in certain crops. We have also observed that when several crops are grown in the same location, certain crops contain these POC residues while other crops do not. For example, in 1990 eight crops were tested that were grown on one farm. Tomatoes and peppers contained no POC residues, but squash, cantaloupe, and beets contained small amounts of chlordane and/or heptachlor epoxide. This farm was a transitional organic farm, and no pesticides had been applied to the crops for at least 3 years. At another farm from which various crops were tested each year from 1991 to 1996, samples of cucumbers, lettuce, and squash contained POC residues, whereas samples of tomatoes and peppers did not. These observations were also noted at 22 other farms and orchards, as well as The Station's Lockwood Farm. At each such site more than two samples were collected, at least one of which contained a residue of a POC pesticide. In all these instances, crops such as squash, cucumbers, lettuce, and beets contained POC residues, while tomatoes, strawberries, snap-beans, and corn did not contain any POC residues.

In Table 3 we list our findings of POC residues in surveillance samples from the past 5 years. For us to draw conclusions from this summary, only those commodities are listed for which a minimum of ten surveillance samples were analyzed. Although DDE was detected in a surveillance sample of collards this year, this crop was not included in Table 3, since ten surveillance samples were not analyzed. Furthermore, in 1990, chlordane and heptachlor epoxide were detected in one cantaloupe sample, but since this was a compliance sample, it also was not included in Table 3. From the data in Table 3 it is apparent that squash was the commodity that most often contained POC pesticide residues, with approximately one-third of all squash samples tested containing residues of either DDE or chlordane. Squash was followed by cucumbers, beets, eggplant, spinach, lettuce, cabbage, carrots, and potatoes. Crops such as strawberries, tomatoes, and other small fruits, along with tree fruits, corn, peppers, and snap-beans, did not contain

any POC residues. From our data, it appears that certain vine and root crops selectively extract POC pesticides from farm land, while other crops that are grown under identical conditions do not.

CONCLUSIONS

The overall summaries of our findings for the past 9 years are detailed in Table 4. Figure 2 illustrates our findings from 1992 to 1996. Our 1996 findings were consistent with past years with approximately 58% of the samples tested containing no pesticide residues. Of the fresh produce tested, 61% was from Connecticut farms and orchards, 29% from other states, and 10% from foreign countries. The results of pesticide residue testing at this Station over the past 7 years are consistent with the testing performed by FDA (Food and Drug Administration, 1995). As in the FDA data, approximately 42% of the samples we tested had detectable quantities of pesticide residues. The percentage of violative samples, 1.8%, was similar to testing performed in other years.

As in earlier years, our findings continue to show that the residues of pesticides found in fruits and vegetables sold in Connecticut are generally well within the safety limits established by EPA.

ACKNOWLEDGMENTS

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Table 1. Summary of pesticides found in fresh fruits and vegetables sold in Connecticut.

COMMODITY	Pesticide	Samples with residues	No. of times detected	Residue range (ppm)	EPA tolerance (ppm)
APPLES (31 samples)		15			
	Captan		2	0.05-0.08	25
	Chlorpyrifos		9	0.012-0.085	1.5
	Dicofol		3	0.10-0.90	5
	Endosulfan		7	0.004-0.044	2.0
	Permethrin		1	0.016	0.05
ASPARAGUS (3 samples)		0			
BANANAS (2 samples)		0			
BEANS, SNAP (5 samples)		2			
	Endosulfan		1	0.12	2
	Vinclozolin		1	0.2[a]	0
BEET ROOTS (4 samples)		1			
	DDE		1	0.003	0.2[b]
BEET TOPS (4 samples)		1			
	DDE		1	0.004	0.2[b]
BLUEBERRIES (14 samples)		4			
	Captan		4	0.01-0.2	25
BROCCOLI (3 samples)		0			
CABBAGE (4 samples)		1			
	DDE		1	0.007	0.5[b]
CARROTS (5 sample)		0			
CELERY (1 sample)		1			
	Chlorothalonil		1	0.15	15
CHERRIES (2 samples)		1			
	Iprodione		1	0.06	20
COLLARDS (1 sample)		1			
	DDE		1	0.01	0.5[b]
CORN (10 samples)		0			
CUCUMBERS (10 samples)		9			
	Chlorothalonil		2	0.02-0.03	5
	DDE		4	0.003-0.01	0.1[b]
	Endosulfan		7	0.002-0.08	2.0
EGGPLANT (3 samples)		2			
	DDE		2	0.008-0.1	0.1[b]

Table 1. Summary of pesticides found in fresh fruits and vegetables sold in Connecticut (continued).

COMMODITY	Pesticide	Samples with residues	No. of times detected	Residue range (ppm)	EPA tolerance (ppm)
ENDIVE (2 samples)		1			
	Chlorothalonil		1	0.5[a]	0
GRAPES (2 samples)		0			
KALE (1 sample)		1			
	DCPA (Dacthal)		1	0.2	5
LETTUCE (15 samples)		6			
	Endosulfan		2	0.02-0.18	2
	DDE		4	0.002-0.006	0.5[b]
NECTARINES (1 sample)		1			
	Iprodione		1	0.2	20
ONIONS (4 samples)		0			
ORANGES (3 samples)		0			
PEACHES (7 samples)		7			
	Captan		2	0.08-0.09	50
	Endosulfan		4	0.01-0.5	2.0
	Iprodione		1	0.5	20.0
	Permethrin		1	0.26	5.0
	Vinclozolin		1	0.006	25
PEARS (15 samples)		6			
	Endosulfan		3	0.005-0.03	2
	Iprodione		1	0.08[a]	0
	Permethrin		2	0.04-0.13	3
	o-Phenylphenol		1	1.0	25
PEAS (3 samples)		0			
PEPPERS, BELL (6 samples)		2			
	Endosulfan		2	0.12-0.15	2
PLUMS (2 samples)		0			
POTATOES (8 samples)		3			
	Chlorpropham		2	0.12-1.6	50
	DDE		1	0.014	1[b]
POTATOES, SWEET (1 sample)		1			
	Dicloran		1	0.02	10
RADISHES (2 samples)		0			
RASPBERRIES (2 samples)		0			

Table 1. Summary of pesticides found in fresh fruits and vegetables sold in Connecticut (continued).

COMMODITY	Pesticide	Samples with residues	No. of times detected	Residue range (ppm)	EPA tolerance (ppm)
SPINACH (6 samples)		2			
	Permethrin		1	0.26	20
	DDE		2	0.01-0.02	0.5[b]
SQUASH, SUMMER (9 samples)		8			
	Chlordane		4	0.05-0.12[c]	0.1[b]
	Chlorothalonil		1	0.021	5
	DDE		2	0.003	0.1[b]
	Dieldrin		1	0.01	0.1[b]
	Endosulfan		3	0.01-0.10	2.0
SQUASH, WINTER (6 samples)		6			
	Chlordane		2	0.1	0.1[b]
	Chlorothalonil		2	0.013	5
	DDE		2	0.01-0.05	0.1[b]
	Dieldrin		1	0.007	0.1[b]
	Vinclozolin		1	0.022[a]	0
STRAWBERRIES (55 samples)		48			
	Captan		24	0.01-8.4	25
	Chlorpyrifos		1	0.004	0.2
	DCPA (dacthal)		7	0.001-0.1	2
	Dicofol		3	0.03-0.83	5
	Endosulfan		22	0.005-0.18	2.0
	Folpet		1	7.3	25
	Iprodione		10	0.01-1.8	15.0
	Methoxychlor		1	0.12	14
	Vinclozolin		20	0.006-1.53	10
TOMATOES (21 samples)		6			
	Chlorothalonil		2	0.01-0.24	5
	DCPA (Dacthal)		1	trace	1
	Endosulfan		5	0.008-0.02	2.0
MISCELLANEOUS (1 sample of each)		0			

Avacadoes, Cantaloupe, Cranberries, Kiwi, Mustard Greens, Parsnips, Rhubarb, Turnips

(a) Residue not allowed on this commodity.
(b) Action Level per FDA Compliance Policy Guidelines (7141.01).
(c) Residue over FDA Action Level.

Table 2. Summary of pesticides found in processed fruits and vegetables sold in Connecticut.

COMMODITY Pesticide	Samples Analyzed	Samples with residues	No. of times detected	Residue range (ppm)
JUICES				
Apple Cider/Juice	31	0		
Miscellaneous Fruit Juices	4	0		
FRUITS & VEGETABLES, CANNED				
Artichokes	1	0		
Oranges	1	0		
Peas	3	0		
VEGETABLES, FROZEN				
Spinach	2	2		
Permethrin			2	0.06-3.6
DDE			2	0.012-0.02
MISCELLANEOUS				
Rice	2	0		
Cabbage, Shredded	1	0		
Carrots, Shredded	1	0		

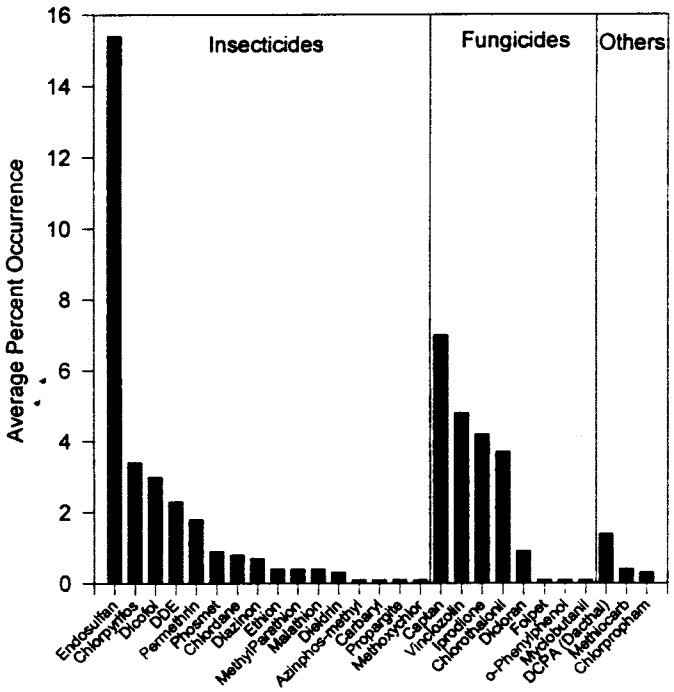

Figure 1. Frequency of pesticide occurrence in fresh produce from 1992-1996.

Table 3. Summary of findings of persistent organochlorinated pesticides (POC) from 1992-1996.

COMMODITY	No. of Samples	No. with Residues	No. with POC Residues	% with POC Residues
Squash, Winter	11	7	5	45%
Squash, Summer	55	31	18	33%
Cucumbers	50	25	10	20%
Beet Roots	16	4	3	19%
Beets Tops	12	3	2	17%
Eggplant	19	6	3	16%
Spinach	24	8	3	13%
Lettuce	55	13	4	7%
Cabbage	20	3	1	5%
Carrots	21	1	1	5%
Potatoes	30	5	1	3%
Apples	260	119	0	0%
Strawberries	195	127	0	0%
Blueberries	124	52	0	0%
Tomatoes	108	26	0	0%
Peaches	58	40	0	0%
Pears	53	21	0	0%
Peppers, Bell	48	18	0	0%
Corn	42	0	0	0%
Beans, Snap	39	11	0	0%
Raspberries	26	15	0	0%
Grapes, Table	24	8	0	0%
Plums	18	9	0	0%
Oranges	18	2	0	0%
Nectarines	16	9	0	0%
Asparagus	15	0	0	0%
Cantaloupe	13	0	0	0%
Broccoli	13	0	0	0%
Mushrooms	13	1	0	0%
Bananas	12	0	0	0%
Peas	12	0	0	0%
Grapefruit	10	1	0	0%

Table 4. Nine year summary of samples tested.

Year	Total Samples Tested [a]	Samples With No Residues	Samples With Residues Within EPA Tolerances [a]	Samples With Residues Over EPA Tolerances [b]	Samples With Residues With No EPA Tolerances [b]
1988	310	165	138	2	5
1989	349	174	170	3	2
1990	436	170	265	0	1
1991	285	188	96	0	1
1992	282	178	99	1	4
1993	441 [b]	305	126 [b]	3	7
1994	545 [b]	414	125 [b]	1	5
1995	444 [b]	307	129 [b]	0	8
1996	327 [b]	188	134 [b]	1 [c]	4
Total	3419	2089	1282	11	37

(a) Includes resamples.
(b) Represents original (surveillance) samples only, does not include (compliance) resamples.
(c) Over FDA action level.

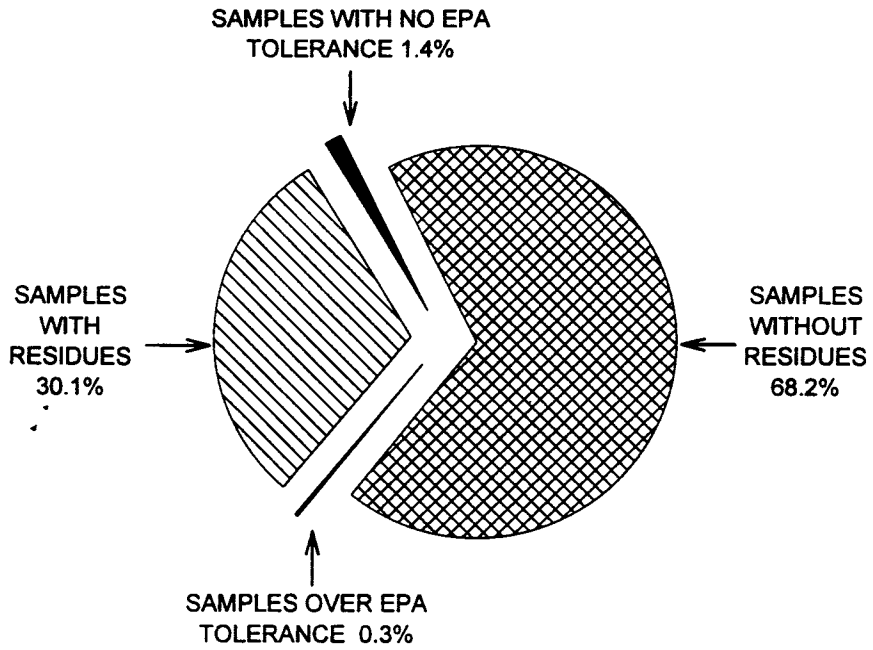

Figure 2. Summary of results from 1992-1996.