The Connecticut Agricultural Experiment Station, New Haven

Pesticide Residues in Produce Sold in Connecticut 1995

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Bulletin 934
May 1996

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

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Crop production has increased dramatically over the past decades due, in part, to the application of pesticides that reduce losses from weeds, insects, and diseases. In recent years public awareness about pesticide residues in foods has become a major consumer safety issue.

Growers have access to a broad and expanding array of agrochemicals (Sine, 1993). Consequently, analytical methodology must be modified in order to detect residues from a constantly changing list of analytes. This presents a formidable challenge, because the actual chemicals that are applied to a crop are generally not known prior to testing. Compounding this situation is the fact that allowable residue levels for pesticides have been decreasing, requiring analytical techniques with greater sensitivity to achieve lower detection levels (Code of Federal Regulations, 1994).

The U.S. Environmental Protection Agency (EPA) sets allowable tolerances for pesticides. Federal agencies, such as the U.S. Food and Drug Administration (FDA), and state agencies, such as the Connecticut Department of Consumer Protection, enforce these tolerances. These regulatory agencies must assure the public that the fruits and vegetables that are offered for sale meet EPA safety regulations (Code of Federal Regulations, 1994). To do this they 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. This testing must also be rapid, since many crops are being sold at the same time they are in the laboratory for testing.

As part of an overall food safety program, the Analytical Chemistry Department at The Connecticut Agricultural Experiment Station, in cooperation with the Connecticut Department of Consumer Protection, collects and analyzes food sold in Connecticut to determine if pesticide residues are within EPA tolerances. This report presents the results of our 1995 market basket study, the improvements and expansion to our testing protocol, and assures consumers that produce grown in this state, other states, and foreign countries meets EPA pesticide tolerance levels.

METHODS

Samples of fresh produce and processed foods from Connecticut, other states, and foreign countries, are collected at various producers, retailers, and wholesale outlets by inspectors from the Connecticut Department of Consumer Protection, and delivered to our laboratory in New Haven within 24 hours of collection. The market basket commodities obtained are referred to 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). Each sample is prepared as received, in its natural unwashed and unpeeled state. The sample is chopped and a portion is blended with organic solvents to extract the pesticides from the sample. A small amount of the extract is then 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.

In 1993, we initiated the use of gas chromatography with a mass selective detector (GC-MSD) to confirm all violative residues, and in 1994, we expanded the use of GC-MSD to include randomly selected samples (Pylypiw et al., 1994, 1995). Mass spectrometry identifies each pesticide by its unique fingerprint fragmentation pattern. This technique has allowed us to identify myclobutanil, a relatively new fungicide used on grapes, and chlorpropham, a sprout inhibitor used on potatoes. Other GC-MSD findings have confirmed

the presence of dicofol on blueberries, excessive amounts of chlorothalonil on peaches, nectarines, and plums, and trace amounts of methiocarb on blueberries. The use of GC-MSD has allowed us to find residues that were not detected by our other gas chromatograph detectors.

RESULTS AND DISCUSSION

In 1995 a total of 444 samples, representing a variety of fresh and processed foods, were tested. Of those 444 samples, 344 (77.5%) were fresh produce, and 100 (22.5%) were processed foods. Pesticide residues were found in 123 samples of fresh produce (35.8%), and 14 (14.0%) samples of processed products. The sample commodities and concentration ranges of all residues found in surveillance samples are given in Tables 1-3 for fresh produce and processed foods. None of the samples tested exceeded EPA tolerances, but eight samples contained residues for which no EPA tolerance exists for that commodity. In response to these surveillance findings, 26 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, which has the responsibility for enforcement of pesticide tolerances.

Two samples, one of lettuce and one of raspberries, contained trace amounts of chlorpyrifos and DCPA (dacthal), respectively (Table 1). Although these pesticides are allowed on other crops, their presence on these commodities, even at trace levels, is not permitted. Two samples of summer squash contained trace amounts of DDE (a soil metabolite of DDT) and chlordane (Table 1). The agricultural use of these organohalogen pesticides in the United States has been banned since 1972; however, they have persisted in the environment (Pylypiw et al., 1991). Even though there is no EPA tolerance for these pesticides, the FDA recognizes their persistence in the environment and has set action levels (allowable amounts) for these compounds in produce (Compliance Policy Guides, 1986). In no sample were these pesticides above the FDA action levels.

Twenty-seven (7.9%) of the fresh produce samples were labeled as "organically grown." When tested, one sample of tomatoes contained a residue of endosulfan (Table 1). The residue was within the EPA tolerance for tomatoes. However, Connecticut Organic Law states that produce labeled as "organically grown" cannot contain detectable pesticide residues (State of Connecticut, General Statutes).

This year, in addition to fresh produce, we tested processed foods such as apple cider, canned and frozen fruits, vegetables, and baby foods (Table 2). Overall, few pesticide residues were found in these food products (14 out of 100 samples), and all residues were below EPA tolerance levels for their respective fresh commodities. Of the few residues found, the fungicide dicloran was found in a sample of baby food, and the insecticides permethrin and endosulfan were found in canned and frozen spinach. Residues of these pesticides are common on fresh samples of these commodities.

In 1994, using GC-MSD, two samples of blueberries were found to contain methiocarb, a bird repellent that was removed from EPA tolerance lists in 1990 (Pylypiw et al., 1995). In response to these findings, in 1995 we initiated testing of all blueberry samples by GC-MSD. Samples were obtained from 25 Connecticut producers and 13 out of state producers. The sample concentration ranges of all residues found in the blueberry samples are given in Table 3. In mid-August 1995, the first finding of methiocarb in a Connecticut blueberry sample occurred and ultimately, samples from six Connecticut blueberry producers were shown to contain detectable levels of methiocarb. In addition to methiocarb, violative residues of chlorothalonil and DCPA (dacthal) were found on Connecticut blueberries (Table 3, surveillance and compliance samples). Chlorothalonil residues were also found on blueberries from New Jersey (Table 3, surveillance samples only). Although chlorothalonil is not registered for use on blueberries, an EPA exemption was granted to New Jersey blueberry growers for control of anthracnose (Pavlis, 1995). Thus, a residue of chlorothalonil on blueberries from New Jersey was not a violation. As a consequence of our residue findings, the FDA had blueberry samples collected in the remaining New England States, as well as in New York and the Pacific Northwest. The FDA found isolated instances of methiocarb usage in New York and Washington State. The FDA has since noted that Connecticut is the only state in New England to have an active, viable pesticide monitoring program in place to respond to circumstances involving the misapplication of pesticides (Rahto, 1996).

Figure 1 shows all pesticides that were found and their frequency of occurrence in fresh produce samples from 1992 to 1995. 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.

The overall summaries of our findings for the past 8 years are detailed in Table 4. Figure 2 illustrates our findings from 1992 to 1995. Our 1995 findings were consistent with past years with approximately 69% of the samples tested containing no pesticide residues. Of the fresh produce tested, 54% was from Connecticut farms and orchards, 33% from other states, and 13% 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 30% of the samples we tested had detectable quantities of pesticide residues. The percentage of violative samples, 2.3%, was slightly higher due to the violative findings of methiocarb on blueberries.

Connecticut consumers may be assured that their food supply is constantly monitored through our market basket survey. 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

Samples were collected by inspector Ellen Sloan and other inspectors from the Food Division of the Department of Consumer Protection.

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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 (68 samples)	35			
Captan		6	0.08-0.24	25
Chlorpyrifos		11	0.02-0.08	1.5
Dicofol		9	0.10-0.64	5
Endosulfan		13	0.004-0.15	2.0
Phosmet		2	0.42-0.98	10
Asparagus (5 samples)	0			
Beans, Snap (12 samples)	6			
Chlorothalonil		4	0.21-1.2	5
Endosulfan		3	0.05-0.10	2.0
Broccoli (4 samples)	0			
Brussels Sprouts (2 samples)	0			
Cabbage (3 samples)	0			
Cantaloupe (3 sample)	0			
Cauliflower (2 samples)	0			
Celery (2 samples)	0			
Corn (4 samples) 0				
Cucumbers (9 samples)	3			
Endosulfan		3	0.01-0.08	2.0
Eggplant (3 samples)	0			
Grapefruit (2 samples)	0			
Grapes (6 samples)	2			
Captan		1	0.18	50
Vinclozolin		1	0.11	6.0
Lettuce (13 samples)	3			
Chlorpyrifos		1	0.01	0[a]
Dicloran		1	0.08	10
Endosulfan		1	0.07	2.0
Permethrin		1	3.4	20.0

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)
Nectarines (4 samples)	1			
Endosulfan		1	0.17	2.0
Oranges (4 samples)	0			
Peaches (15 samples)	10			
Captan		1	1.8	50
Diazinon		1	0.04	0.7
Dicofol		1	0.10	10
Endosulfan		6	0.02-0.83	2.0
Iprodione		4	0.20-0.60	20.0
Permethrin		1	0.17	5.0
Pears (11 samples)	4			
Azinphos-methyl		1	1.1	0.5
Endosulfan		2	0.01-0.85	2.0
Phosmet		1	0.5	10
Peas (5 samples)	0			
Peppers, Bell (10 samples)	4			
Diazinon		1	0.04	0.5
Endosulfan		2	0.07-0.09	2.0
Permethrin		1	0.08	1.0
Plums (2 samples)	0			
Potatoes (8 samples)	0			
Raspberries (6 samples)	3			
Captan		1	0.15	25
DCPA (dacthal)		1	0.01	0[a]
Iprodione		3	0.13-2.7	15.0
Vinclozolin		2	0.05-0.06	10.0
Scallions (2 samples)	0			
Spinach (3 samples)	0			
Squash, Summer (6 samples)	4			
Chlordane		2	0.02-0.03	0.1[b]
DDE		1	0.03	0.1[b]
Endosulfan		2	0.02-0.05	2.0

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)
Strawberries (26 samples)	20			
Captan		10	0.11-7.5	25
DCPA (dacthal)		3	0.01-0.04	2
Diazinon		1	0.20	0.5
Dicofol		2	0.18-0.27	5
Endosulfan		5	0.01-0.07	2.0
Iprodione		3	0.05-1.4	15.0
Vinclozolin		12	0.01-0.60	10
Tangerines (2 samples)	0			
Tomatoes (27 samples)	6			
Chlorothalonil		2	0.11-1.4	5
Endosulfan		4	0.01-0.10	2.0
Permethrin		1	0.07	2
Turnip Greens (1 sample)	1			
Endosulfan		1	1.3	2.0
Miscellaneous (1 sample of each)	0			

Alfalfa Sprouts, Artichokes, Bananas, Bean Sprouts, Beets, Beet Tops, Blackberries, Bok Choy, Broccoli Rabe, Carrots, Cranberries, Dandelion Greens, Escarole, Leeks, Lemons, Mangoes, Mushrooms, Mustard Greens, Onions, Parsnips, Pumpkins, Radishes, Winter Squash, Yams

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

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	36	0		
Miscellaneous Fruit Juices	5	0		
Fruit, Canned				
Apple Pie Filling	2	0		
Grape Jelly	1	0		
Fruit, Dried				
Dates	1	0		
Raisins	2	0		
Vegetables, Canned				
Beans, green	1	0		
Beets	4	0		
Carrots	2	0		
Mushrooms	1	0		
Peas	2	0		
Peppers	7	4		
Permethrin			4	0.02-0.75
Endosulfan			1	0.12
Potatoes	1	0		
Spinach	4	2		
Permethrin			2	0.23-1.0
Tomato Products	4	0		
Vegetables, Chopped/Shredded				
Broccoli	1	0		
Cabbage	1	0		
Carrots	2	0		
Cauliflower	1	0		
Lettuce	1	0		
Radishes	1	0		
Vegetables, Frozen				
Beans, green	1	0		
Broccoli	1	0		
Spinach	9	7		
Permethrin			7	0.23-9.5
Baby Food				
Fruits	1	0		
Vegetables	3	1		
Dicloran			1	0.03
Miscellaneous				
Cereal	1	0		
Crackers	1	0		
Macaroni	3	0		

Table 3. Summary of pesticides found in blueberries sold in Connecticut.

Commodity / Pesticide	Samples with residues	No. of times detected	Residue range (ppm)	EPA tolerance (ppm)
Surveillance (6 violations)				
Blueberries (50 samples)	21			
Captan		6	trace-0.93	25
Carbaryl		1	trace	10
Chlorothalonil		6	0.10-0.48	0[a]
DCPA (dacthal)		1	0.02	0[b]
Endosulfan		4	0.01-0.05	0.1
Malathion		4	0.58-1.3	8
Methiocarb		5	0.03-9.8	0[b]
Phosmet		2	0.91-1.4	10
Compliance (14 violations)				
Blueberries (25 samples)	17			
Captan		3	0.54-1.0	25
Carbaryl		7	trace	10
Chlorothalonil		4	trace-6.0	0[c]
DCPA (dacthal)		7	trace-0.01	0[b]
Endosulfan		2	0.02	0.1
Methiocarb		10	0.29-3.4	0[b]
Methoxychlor		1	1.0	14

(a) No violation, regional tolerance for NJ grown blueberries.
(b) Residue not allowed on this commodity.
(c) Violation, all grown in Connecticut.

Table 4. Eight year summary of samples tested.

Year	Samples Tested [a]	Samples Within EPA Tolerances [a]	Samples Over EPA Tolerances [b]	Samples with No EPA Tolerances [b]
1988	310	138	2	5
1989	349	170	3	2
1990	436	265	0	1
1991	285	96	0	1
1992	282	99	1	4
1993	441 [b]	126 [b]	3	7
1994	545 [b]	125 [b]	1	5
1995	444 [b]	129 [b]	0	8
Total	3092	1148	10	33

(a) Includes resamples.
(b) Represents original (surveillance) samples only, does not include (compliance) resamples.

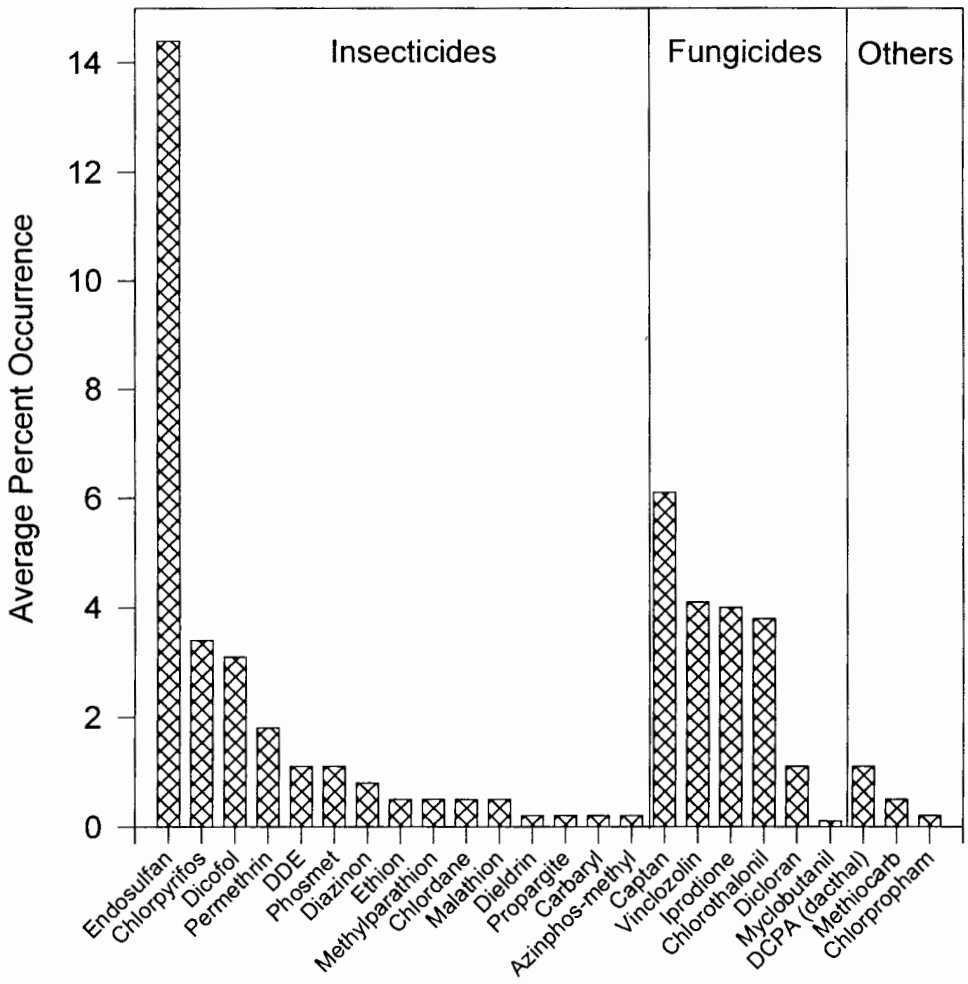

Figure 1. Frequency of pesticide occurrence in fresh produce from 1992 to 1995.

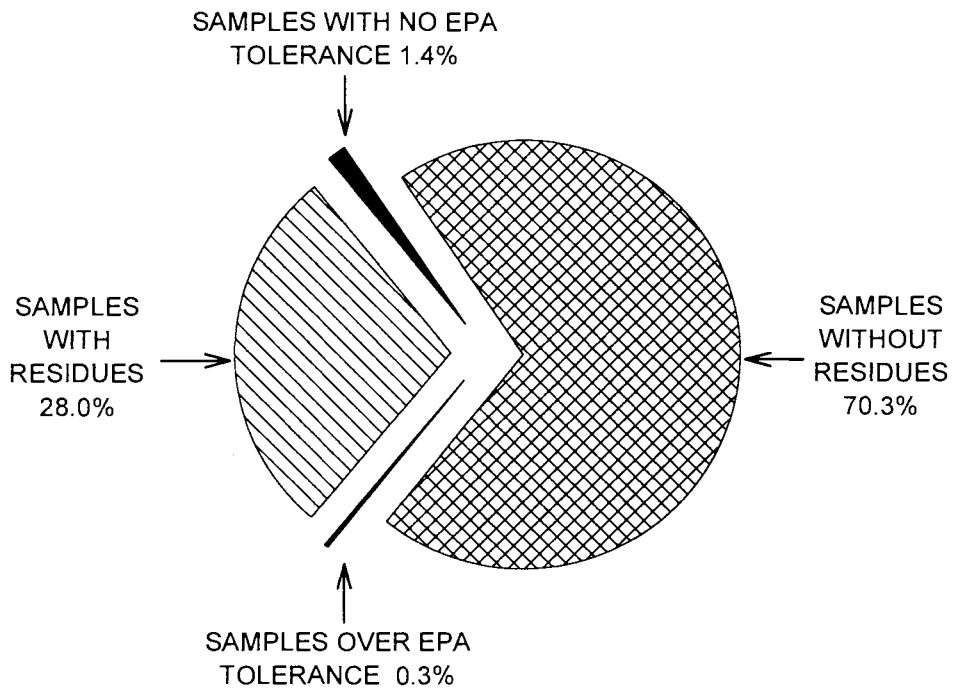

Figure 2. Summary of results from 1992-1995.

The Connecticut Agricultural Experiment Station, founded in 1875, is the first experiment station in America. It is chartered by the General Assembly to make scientific inquiries and experiments regarding plants and their pests, insects, soil and water, and to perform analyses for State agencies. The laboratories of the Station are in New Haven and Windsor; its Lockwood Farm is in Hamden. Single copies of bulletins are available free upon request to Publications; Box 1106; New Haven, Connecticut 06504. ISSN 0097-0905