The Connecticut Agricultural Experiment Station, New Haven

Pesticide Residues in Produce Sold in Connecticut 1994

BY HARRY M. PYLYPIW JR., TERRI MISENTI, AND MARY JANE INCORVIA MATTINA

Bulletin 928

June 1995

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

Pesticide Residues in Produce Sold in Connecticut 1994

BY HARRY M. PYLYPIW JR., TERRI MISENTI, AND MARY JANE INCORIVA MATTINA

Crop production has increased dramatically over the past five decades due largely to the use of agricultural chemicals. These agro-chemicals are collectively known as pesticides and their benefits in controlling plant pests and diseases are well known. However, increasing public awareness about pesticide impact on human health has made consumer safety the overriding issue in pesticide use on crops. In response to widespread concern about the food we eat and its effect on our health, the Analytical Chemistry Department has increased the emphasis on its Food Safety program.

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, 1994). The determination of pesticide residues in fruits and vegetables is a formidable task because there are many pesticides and the actual chemicals used on a crop are seldom known. The Connecticut Agricultural Experiment Station, in cooperation with the Connecticut Department of Consumer Protection, collects and analyzes fruits and vegetables sold in Connecticut to determine if residues are within EPA tolerances. The sampling program is a market-basket survey, targeting products that are for sale to the general public. This report presents the results of our 1994 market basket study on pesticide residues found in produce sold in Connecticut. These results assure consumers that produce grown in this state, other states, and foreign countries meets EPA pesticide tolerance levels.

METHODS

Samples of produce grown in Connecticut, other states, and foreign countries, are collected at various Connecticut producers, retailers, and wholesale outlets by an inspector from the Connecticut Department of Consumer Protection. The samples collected can be classified as either surveillance or compliance, and are brought to our laboratory in New Haven for pesticide residue testing. Most samples that are collected are of the surveillance category, with no prior knowledge of any pesticide application. Compliance samples are obtained as a follow-up to the finding for confirmation of violative pesticide residues.

Commodities are tested for pesticides using a multi-residue method developed in our laboratories (Pylypiw, 1993). Each sample is prepared in its natural state as received, unwashed and unpeeled. The sample is chopped and a portion is placed into a blender. Organic solvents are added to the container to extract the pesticides from the sample. Interfering coextracted compounds, such as organic acids, are removed from the solvent with water. A small amount of the solvent is then injected into various gas chromatographic instruments 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.

RESULTS AND DISCUSSION

In 1994 a total of 545 samples representing a wide variety of fresh and processed produce were tested. Of those 545 samples, 365 (65.3%) were fresh produce, and 189 (34.7%) were processed foods. Pesticide residues were found in 115 samples of fresh produce (31.5%), and 16 (8.5%) samples of processed products. For all but six samples of produce, the pesticide residues were within EPA tolerances. In response to these initial findings, 40 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. The sample commodities and concentration ranges of all residues found are given in Table 1 for fresh produce and Table 2 for processed foods.

A sample of peaches from a Connecticut orchard contained an excess of chlorothalonil above EPA tolerances. Twenty-two compliance samples of peaches, plums, nectarines, apples, and pears were obtained from this orchard. Two samples of blueberries contained trace amounts of methiocarb, a bird repellent that has been banned from use since 1990. Three other samples, one each of beets, beet tops, and eggplant, contained traces of pesticides that were not allowed on those commodities. To summarize, 1.6% of the fresh produce samples tested contained violative residues.

Ten samples, five each of spinach, two each of cucumbers and squash, and one each of carrots and eggplant, contained either a trace of DDE (a soil metabolite of DDT), chlordane, or dieldrin (see Table 1). The agricultural use of these organohalogen pesticides has been banned in the United States since 1972; however, they have persisted in the environment (Pylypiw et al., 1991). Although 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). No sample that contained these pesticides was above the FDA action levels.

This year we have increased the number of samples of fresh produce tested in our pesticide residue program and included more processed foods (see Table 2). In past years we have tested some processed foods, most notably apple cider and a few samples of dried fruits. This year we have expanded the sampling to include canned and frozen fruits, vegetables, and fruit juices along with apple cider, dried fruits, and baby foods. Overall, few pesticide residues were found in these food products (16 out of 189 samples), and all residues were below EPA tolerance levels or FDA action levels for the respective fresh commodity. Of the few residues found, the fungicides, iprodione and captan, were present at low levels in several canned and frozen fruit samples, and the insecticide, permethrin, was found, also at low levels, in canned and frozen leafy green vegetables. Residues of these pesticides are common on fresh samples of these commodities.

In 1993, we initiated the use of gas chromatography with a mass selective detector (GC-MSD) to confirm all violative residues and to identify unknown peaks in our chromatograms. In a continuing effort to improve our testing during 1994, we expanded the use of mass spectrometry to include routine GC-MSD analysis of randomly selected samples. Mass spectrometry identifies each pesticide by its unique fingerprint fragmentation pattern. For example, in a sample of California grapes an unknown peak was found in the chromatograms from our usual GC detectors. Analysis of this extract by GC-MSD identified the peak as myclobutanil, a relatively new fungicide, registered for use on grapes. Another example involved routine screening of blueberry samples. The use of GC-MSD on this crop allowed us to find a residue of the carbamate insecticide methiocarb, that was not detected by our other GC detectors. Methiocarb is a bird repellent that was removed from EPA tolerance lists in 1990, and several fruit growers were illegally using this pesticide. Two samples were found to contain this pesticide. Use of GC-MSD is part of an ongoing research effort to identify pesticide residues and is now a significant part of pesticide residue testing.

Figure 1 shows all pesticides that were found and their frequency of occurrence in the 1994 analyses. Of particular interest are the pesticides that are most often found in our survey. As in past years, the insecticide endosulfan was the most frequently detected residue in all commodities tested. Also of note, the highest residue of this pesticide was 0.25 ppm, 13% of the allowable amount for that commodity. Other pesticides that were frequently detected were iprodione, captan, and permethrin. In 31 samples (5.7%) more than one residue was found. This usually occurred on fruits, especially strawberries, apples, and peaches.

The overall summaries of our findings for the past seven years are detailed in Table 3. Our 1994 findings were consistent with past years with roughly 76% of the samples tested containing no pesticide residues (Figure 2) (Pylypiw, et al., 1994). Most of the fresh produce tested, 55.3%, was from Connecticut farms and orchards, 29.5% from other states and 14.0% from foreign countries. The results of pesticide residue testing at this Station over the past seven years are consistent with the testing performed by FDA (Food and Drug Administration, 1994). Like the FDA approximately 40% of the samples we test contain detectable quantities of pesticide residues. The percentage of violative samples is approximately 2%, which is also consistent with FDA testing programs.

Improvements to our pesticide residue program include increased sampling of fresh and processed foods, and the use of GC-MSD to analyze for more pesticides. The 1994 data along with the data from past years confirm the safety of the food supply. Consumers should be assured that their food supply is constantly tested, and the benefits of eating fruits and vegetables far outweigh any potential dangers from pesticides. 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 Ellen Sloan, an inspector from the Food Division of the Department of Consumer Protection.

REFERENCES

Code of Federal Regulations (1994) Title 40, U.S. Government Printing Office, Washington, DC, Sections: 180-186.

Compliance Policy Guidelines (1986) Food and Drug Administration, Office of Enforcement, Division of Compliance Policy, Chapter 41, Guide 7141.01, p. 2.

Food and Drug Administration (1994) Food and Drug Administration Pesticide Program—Residue Monitoring—1993. J. AOAC Int., 77:161A-185A.

Pylypiw, H.M., Jr., Misenti, T., Mattina, M.J.I. (1994) Pesticide Residues in Produce Sold in Connecticut 1993. Bulletin 917, The Connecticut Agricultural Experiment Station, New Haven, CT.

Pylypiw, H.M, Naughton, E. Hankin, L. (1991) DDT Persists in Soil: Uptake by Squash Plants. J. Dairy, Food and Environ. Sanit., 11:200-201.

Pylypiw, H.M., Jr. (1993) Rapid Gas Chromatographic Method for the Multiresidue Screening of Fruits and Vegetables for Organochlorine and Organophosphate Pesticides. J. AOAC Int., 76:1369-1373.

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 (64 samples)	24			
Captan		4	0.02-0.06	25
Carbaryl		1	0.07	10
Chlorpyrifos		2	0.025-0.04	1.5
Dicofol		7	0.03-0.46	5
Endosulfan		13	0.01-0.08	2
Methoxychlor		2	0.14-0.25	14
Propargite		2	0.65-1.9	3
Asparagus (1 sample)	0			
Avocadoes (1 sample)	0			
Bananas (6 samples)	0			
Beans, Snap (6 samples)	1			
Chlorothalonil		1	0.15	5
Endosulfan		1	0.05	2
Beans, Fava (1 sample)	0			
Beets (6 samples)	1			
Endosulfan		1	0.02[a]	0
Beet Tops (4 samples)	1			
Endosulfan		1	0.06[a]	0
Blueberries (23 samples)	8			
Captan		3	0.03-0.10	25
Chlorothalonil		2	0.07-0.45	1.0
Endosulfan		3	0.01-0.04	0.1
Iprodione		2	0.2	15
Methiocarb		2	0.43-0.60[a]	0
Broccoli (3 samples)	0			
Broccoli Rabe (1 sample)	1			
DCPA		1	0.2	5
Brussels Sprouts (1 sample)	0			
Cabbage (2 samples)	0			
Carrots (7 samples)	1			
DDE		1	0.08	3.0[b]
Cauliflower (4 samples)	0			
Chard, Swiss or Red (2 sample)	0			
Cherries (1 sample)	0			
Chickory (1 sample)	0			
Clementines (3 samples)	1			
Captan		1	0.05	25
Corn (5 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)
Cranberries (1 sample)	0			
Cucumbers (16 samples)	6			
Chlordane		1	0.01	0.1[b]
Chlorpyrifos		1	0.08	0.1
DDE		1	0.02	0.1[b]
Dieldrin		1	0.02	0.1[b]
Endosulfan		4	0.007-0.06	2
Eggplant (6 samples)	3			
DDE		1	0.01	0.1[b]
Diazinon		1	0.12[a]	0
Endosulfan		1	0.04	2
Permethrin		1	0.20	1
Endive (1 sample)	0			
Grapes, Table (11 samples)	4			
Iprodione		2	0.1-0.2	60
Methyl parathion		2	0.09-0.15	1
Myclobutanil		1	0.15	1
Grapes, Wine (1 sample)	1			
Iprodione		1	0.22	60
Greens, Mustard (1 sample)	1			
Endosulfan		1	0.02	2
Permethrin		1	2.0	20
Kale (1 sample)	0			
Kiwifruit (1 sample)	1			
Vinclozolin		1	0.05	10
Lettuce (12 samples)	3			
Diazinon		1	0.11	0.7
Endosulfan		1	0.005	2
Permethrin		1	1.5	2
Limes (1 sample)	1			
Ethion		1	0.13	5
Mangoes (1 sample)	0			
Melons (4 samples)	1			
Endosulfan		1	0.03	2
Mushrooms (1 sample)	0			
Nectarines (6 samples)	4			
Dicloran		1	0.2	20
Endosulfan		1	0.01	2
Iprodione		2	0.3-0.39	20
Onions (1 sample)	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)
Oranges (3 samples)	2			
Chlorpyrifos		1	0.07	1
Ethion		1	0.13	5
Parsnips (2 samples)	0			
Peaches (16 samples)	9			
Captan		3	0.1-0.5	50
Chlorothalonil		1	15[c]	0.5
Chlorpyrifos		1	0.03	0.05
Dicloran		1	0.15	20
Endosulfan		4	0.03-0.25	2
Iprodione		4	0.03-1.0	20
Pears (12 samples)	4			
Captan		2	0.1-0.33	25
Endosulfan		2	0.006-1.0	2
Peas (3 samples)	0			
Peppers, Bell (9 samples)	3			
Chlorpyrifos		1	0.06	1
Endosulfan		2	0.04-0.08	2
Permethrin		1	0.10	1
Peppers, Hot (1 sample)	0			
Plaintains (1 sample)	0			
Plums (7 samples)	4			
Endosulfan		1	0.02	2
Iprodione		3	0.04-0.6	20
Potatoes (2 samples)	0			
Radishes (2 samples)	0			
Radishes, Daikon (1 sample)	0			
Radish Tops (1 sample)	0			
Raspberries (4 samples)	2			
Captan		1	1.7	25
Vinclozolin		1	3.5	10
Spinach (5 samples)	2			
DDE		1	0.04	0.5[b]
Endosulfan		1	0.32	2
Squash, Summer (17 samples)	8			
Chlordane		1	0.05	0.1[b]
Chlorothalonil		4	0.04-0.06	5
Diazinon		2	0.01-0.05	0.5
Dieldrin		1	0.01	0.1[b]
Endosulfan		3	0.01-0.03	2

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 (41 samples)	14			
Captan		3	0.24-2.8	25
Chlorpyrifos		1	0.06	0.5
Dicofol		1	0.3	5
Endosulfan		6	0.02-0.05	2
Iprodione		4	0.28-1.7	15
Vinclozolin		7	0.02-0.13	10
Tangerines (1 sample)	0			
Tomatoes (19 samples)	4			
Chlorothalonil		1	0.2	5
Chlorpyrifos		1	0.05	0.5
Endosulfan		3	0.005-0.1	2
Permethrin		2	0.06-0.08	2
Turnips (1 sample)	0			
Yams (1 sample)	0			

(a) Residue not allowed on this commodity.

(b) Action Level per FDA Compliance Policy Guidelines (7141.01).

(c) Residue over EPA limit.

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	44	1		
Carbaryl			1	0.01
Cranberry Juice and Blends	9	0		
Grape Juice	6	0		
Grapefruit Juice/Concentrates	6	0		
Lemonade/Concentrates	8	0		
Orange Juice/Concentrates	8	0		
Pineapple Juice	6	1		
Endosulfan			1	0.03
Tomato and Vegetable Juice	7	0		
Miscellaneous Fruit Juices	5	0		
FRUIT, CANNED				
Apple Sauce	4	0		
Blackberries	2	2		
Iprodione			2	0.05-0.73
Cherries	4	0		
Miscellaneous	4	0		
FRUIT, DRIED				
Prunes	2	1		
Iprodione			1	0.23
Raisins	3	0		
FRUIT, FROZEN				
Raspberries	1	1		
Captan			1	0.34
Iprodione			1	1.1
Strawberries	1	1		
Iprodione			1	0.18
VEGETABLES, CANNED				
Carrots	2	0		
Leafy Green Vegetables	4	2		
Permethrin			2	0.13-1.2
Spinach	5	2		
Permethrin			2	0.09-0.17

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

Commodity Pesticide	Samples Analyzed	Samples with residues	No. of times detected	Residue range (ppm)
Sweet Potatoes and Yams	4	0		
Tomato Products	11	0		
VEGETABLES, FROZEN				
Asparagus	1	0		
Cole Crops (Brassica)	6	0		
Legumes	8	0		
Carrots	3	0		
Leafy Green Vegetables	2	1		
Permethrin			1	4.5
Okra	1	0		
Peppers	2	0		
Spinach	7	4		
Chlorpyrifos			1	0.03
DDE			4	0.03
Permethrin			4	0.45-5.0
Turnips	1	0		
BABY FOOD				
Fruits	2	0		
Vegetables	7	0		
MISCELLANEOUS				
Iced Tea	1	0		
Spaghetti Sauce	2	0		

Table 3. Seven 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
Total	2648	1019	10	25

(a) Includes resamples.

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

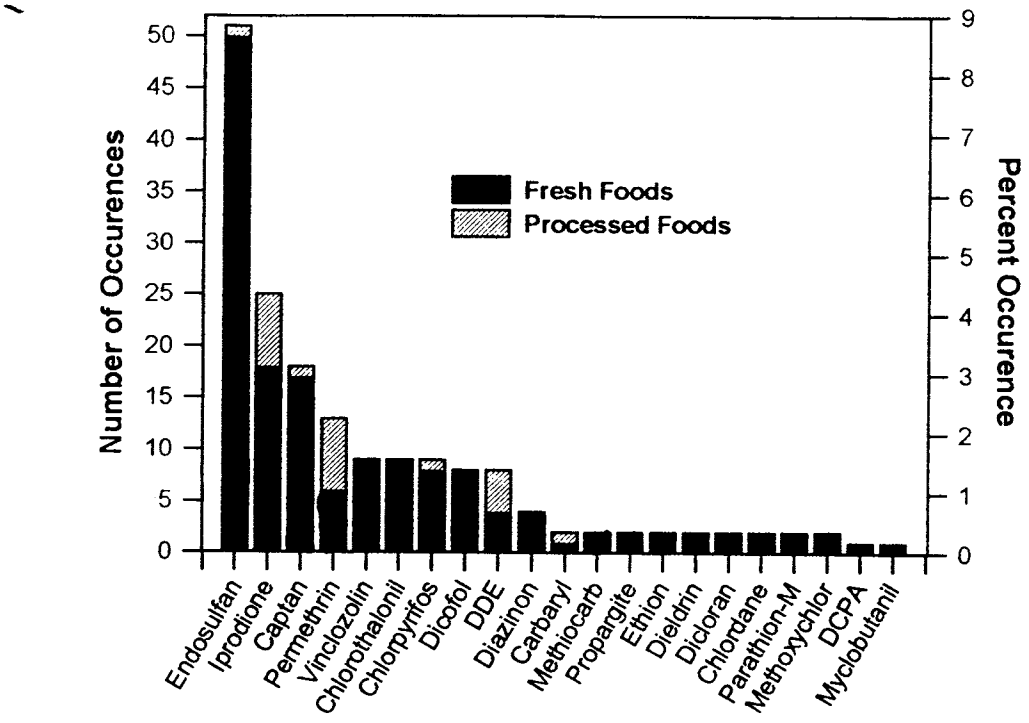

Figure 1. Pesticide occurences on fresh and processed foods. Percent occurence is based on 545 samples.

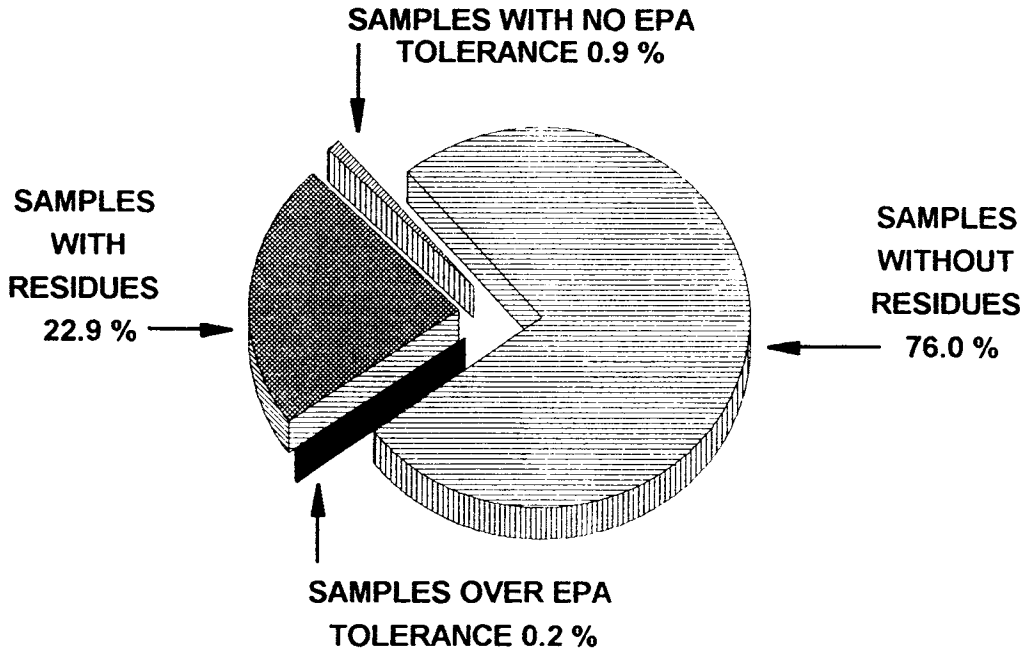

Figure 2. Summary of 1994 results.

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