The Connecticut Agricultural Experiment Station, New Haven

Pesticide Residues in Produce Sold in Connecticut 2001

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In the United States three federal government agencies share responsibility for the regulation of pesticides: The Environmental Protection Agency (EPA), The Food Safety Inspection Service of the United States Department of Agriculture (FSIS-USDA), and the Food and Drug Administration (FDA). It is the responsibility of the EPA to register (*i.e.,* approve) and set tolerances for the use of a particular pesticide which may result in residues on food (CFR, 1999). A tolerance is defined as the maximum quantity of a pesticide residue permitted on a raw agricultural commodity. Tolerances impact food safety by limiting the concentration of a pesticide residue allowed on a commodity and by limiting the type of commodity on which the pesticide is allowed. Tolerances are the only tool the EPA has under the law to control the quantity of pesticides on the food we consume.

The FSIS branch of the USDA is responsible for monitoring and enforcing tolerances of pesticide residues on meat, poultry and certain egg products. The FDA is charged with enforcing tolerances in imported and domestic foods (predominantly fresh fruits and vegetables); and in this state, the Connecticut Department of Consumer Protection (DCP) is responsible for enforcing these tolerances. FDA focuses its sample collection on those states with large agricultural production, such as California and Florida, and these states have implemented their own programs to complement the federal programs. Since 1995 the FDA has only analyzed six samples from Connecticut (FDA, 1995-1999). In 1987, The Connecticut Agricultural Experiment Station (CAES), in conjunction with the DCP, established a program to analyze produce offered for sale in Connecticut for pesticide residue to compliment the monitoring by the FDA. To be able to enforce the EPA-mandated tolerances, regulatory agencies must know the quantity and the type of pesticide residue present in foodstuffs offered for sale.

The FDA approach to pesticide residue monitoring involves samples of individual lots of domestically-produced and imported foods collected as close as possible to their point of entry into the distribution system. Imported samples are collected where they enter U.S. commerce. Samples are analyzed for pesticide residues to enforce the tolerances set by the EPA. The FDA emphasizes raw agricultural commodities analyzed in a raw, unpeeled and unprocessed state, but also analyzes some processed foods. When illegal pesticide residues are found, the FDA can impose various sanctions, including seizure or injunction. For imported produce, shipments are stopped at the port of entry if found to contain illegal residues. If there is reason to believe that future lots from a particular foreign grower or geographic region may be in violation during a given season the FDA can invoke detention without physical examination (automatic detention). In this case, the produce is detained at the port of entry until analysis is complete (FDA, 1995-1999).

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 DCP. The samples are brought to our laboratory in New Haven for pesticide residue testing. These market basket samples are collected without prior knowledge of any pesticide application.

Commodities are tested for pesticides using a multi-residue method developed in our laboratories (Pylypiw, 1993). In most cases, 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 and the mixture is blended to extract the pesticides. Interfering coextracted compounds, such as organic acids, are removed from the solvent extract with water. A small amount of the extract 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.

In an effort to remain current with new pesticide registrations, the Department of Analytical Chemistry at the CAES must continually update the methodology to detect these pesticides. In 2001 the pesticides bifenthrin, diphenylamine, fenhexamid, fenpropathrin, and propiconazole, were all detected and reported for the first time. In addition, sulfur, commonly known as brimstone, is now included in the results of the Connecticut market basket survey.

RESULTS AND DISCUSSION

In 2001 a total of 315 samples representing a wide variety of produce were tested. Of these 229 (73%) samples were fresh produce and 86 samples (27%) were processed foods. Pesticide residues were found in 108 samples or 47% of the fresh produce and 6 samples or 7% of the processed foods (see Tables 1 and 2). The 47% found in fresh produce correlates well with the average of 43% found in fresh produce samples analyzed in our laboratories since 1990. The 6% for processed foods was lower than the average value of 18% found in processed foods since 1990.

Of the samples analyzed in 2001 only two samples, just over one-half of one percent (0.6%), were found to contain pesticide residues that were violative. This is slightly lower than the 0.7% violative residues found in 2000, and lower than the average value of 1% violative samples found in our survey over the past 12 years. One sample of fresh produce, specifically blueberries, grown within the state was found to contain residues of the fungicide *o*-phenylphenol at a concentration of 0.003 parts per million (ppm). *o*-Phenylphenol is not allowed on blueberries, and this finding resulted in a “no tolerance” violation. The second violation was found in a sample of processed food, specifically canned mustard greens, in which residues of the insecticide permethrin were found at a concentration of 12 ppm. Permethrin is not allowed on mustard greens, and this also resulted in a “no tolerance” violation. All violations are immediately reported to DCP, which has the responsibility for enforcing pesticide tolerances within the state of Connecticut. As a direct result of these analyses, DCP issued a recall of mustard greens from retail stores in Connecticut and placed an embargo on the product at the distributor in Connecticut. After a follow-up analysis was conducted at CAES, all recalled and embargoed mustard greens (all lots) were destroyed. The Connecticut DCP forwarded the results to FDA for follow-up at the out-of-state distributor.

In 2001 seven samples (2.2%) of produce were found to contain either residues of DDE, a soil metabolite of DDT, chlordane, or heptachlor epoxide. This number of persistent organohalogen pesticides (POPs) is slightly lower than the average of 3.6% found annually on food crops in our survey since 1990. The use of POPs on food crops was banned in the United States in 1978. Residues of these pesticides continue to persist in the environment, and their uptake and accumulation by crops such as squash, cucumbers and carrots have been well documented (Pylypiw, et al., 1991; Pylypiw et al., 1997; Mattina et al., 2000). In 2001 DDE was found in one cucumber sample grown within Connecticut, one cucumber sample grown in Georgia, and one squash sample grown in Mexico. Additionally, three samples of processed spinach grown outside Connecticut were found to contain DDE. Chlordane and heptachlor epoxide were found in a single squash sample grown in Florida. Heptachlor epoxide is a metabolite of heptachlor, which was a component of technical chlordane. Heptachlor was also used alone as an insecticide. The FDA has set action levels (allowable amounts) for these residues in produce (Duggan, 1998). No sample that contained DDE, chlordane, or heptachlor epoxide was above the FDA action level.

A total of 165 pesticide residues were found on 114 samples of processed and fresh produce in 2001, and 201 samples contained no pesticide residues. The most commonly found pesticides were the insecticide endosulfan and the fungicide captan. Endosulfan, found 43 times in 2001 over a wide variety of fresh produce, accounted for 26% of the residues found during the past year and has accounted for 27% of the residues found since 1990. Captan was found 32 times in 2001 over a wide variety of fresh produce and, as in previous years, no processed produce contained captan. Captan accounted for 19% of the residues found during the past year, and has accounted for 14% of our findings since 1990. It is interesting to note that captan has only been found once on processed produce during the past 11 years. Produce is routinely washed with water during processing to remove loose dirt. A recent study conducted in our laboratories (Krol et. al., 2000) has shown that residues of captan are dramatically reduced by rinsing produce under running tap water for thirty seconds. Sulfur was the third most commonly found pesticide, accounting for 9% of the residues found during the past year.

GENERALLY RECOGNIZED AS SAFE (GRAS) PESTICIDES

While sulfur has been detected in our laboratories in the past, it has not been included in this bulletin until this year. Sulfur is classified as an ‘Other Pesticide Chemical’ by the FDA and falls in the same category as petroleum distillates and insecticidal soaps. These chemicals are produced primarily for other uses but are also used as pesticides. Sulfur is widely used in agriculture as a both a fungicide, against such plant diseases such as powdery mildew, and as

an acaricide, against such pests as mites and leafhoppers. It is also used as a plant and soil amendment. Under the Code of Federal Regulations (CFR, 1999) section 180.2 sulfur is listed as a pesticide that is Generally Recognized as Safe (GRAS) and as such is exempt from tolerance.

It is noteworthy that the use of such pesticides as sulfur, horticultural oil and insecticidal soap are permitted on certified organic produce. In 2001, CAES analyzed four samples of organically grown grapes containing residues of sulfur ranging from 1.2 to 82 ppm. In the past organic certification was granted by various agencies, such as the Northeast Organic Farmers Association (NOFA), based upon the policies of that agency. Due to the differences in practices, attitudes and philosophies of those involved in the organic movement, organic producers recognized the need for standardization in the industry. In 1989 a bill was introduced into Congress to create national organic standards, and in 2001, the final rule was passed establishing the National Organic Program (NOP) as law (CFR, 2001). This law defines the term *organic* as "A labeling term that refers to an agricultural product produced in accordance with the Act and regulations in this part," and establishes national guidelines for producing organic food and for the labeling of produce as organic. Based upon the federal NOP the grape samples containing residues of sulfur were not violative.

CONCLUSIONS

In summary, our market basket survey findings over the past year show that 36% of the samples analyzed contained pesticide residues and that 1% of these were violative. It also indicates that during the past 12 years of our survey, 35% of the 3980 samples analyzed contained at least one pesticide residue and that only about 1% of these were violative. The federal programs run by FDA and USDA help to ensure the safety of our national food supply. However, since neither of these agencies routinely collects samples of locally grown produce, our program supplements these programs by testing Connecticut grown commodities.

The results of our annual market basket survey are in excellent agreement with similar surveys conducted by other regulatory agencies (See Figure 1, Table 4). The percentage of samples containing residues and violations is remarkably similar to those found by the FDA (FDA, 1999), and the states of California (California Residue Monitoring, 1999) and Florida (Florida Division of Food Safety, 2001). Even more remarkable may be the fact that overseas laboratories in countries such as Portugal (Portugal, 1999) find similar percentages of samples containing residues and similar violation rates. Consistently in all these surveys, approximately 36% of the samples tested contained at least one pesticide residue. About 1% of the produce tested which originated in the United States contained violative pesticide residues, while approximately 4% of the produce tested which originated outside of the United States contained violative pesticide residues. Due to the higher number of foreign violative samples, it is important to continue this market basket survey and to increase the number of imported samples analyzed in the survey.

ACKNOWLEDGMENTS

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Table 1. Summary of pesticides found in fresh fruits and vegetables sold in Connecticut, 2001.

Commodity (total samples) Pesticide	Samples with Residues	No. of Times Detected	Residue Range (ppm)	EPA Tolerance (ppm)
Apples (29 samples)	14			
Captan		7	0.01-0.38	25
Diphenylamine		4	0.34-2.2	10
Endosulfan		3	0.072-0.1	2.0
Fenpropathrin		1	1.3	5.0
Methoxychlor		1	0.56	14
Permethrin		1	0.02	0.05
Phosmet		1	0.6	10
Apricots (1 sample)	1			
Captan		1	3.8	50
Asparagus (6 samples)	0			
Beans, Snap (3 samples)	1			
Chlorothalonil		1	0.22	5.0
Endosulfan		1	0.007	2.0
Sulfur		1	0.77	- [(a)]
Blueberries (16 samples)	8			
Captan		4	0.032-0.92	25
Endosulfan		3	0.046-0.05	0.1
Iprodione		1	0.32	15.0
Malathion		2	0.034-0.13	8.0
o-Phenylphenol		1	0.003	0[(b)]
Broccoli (2 samples)	0			
Brussels Sprouts (1 sample)	1			
Endosulfan		1	0.11	2.0
Cauliflower (3 samples)	0			
Celery (3 samples)	0			
Cherries (5 samples)	2			
Carbaryl		1	0.044	10
Sulfur		2	0.054-1.9	- [(a)]

Table 1. (Cont.) Summary of pesticides found in fresh fruits and vegetables sold in Connecticut, 2001.

Commodity (total samples) / Pesticide	Samples with Residues	No. of Times Detected	Residue Range (ppm)	EPA Tolerance (ppm)
Corn (4 samples)	0			
Cucumbers (8 samples)	5			
Chlorothalonil		1	0.036	5
DDE		2	0.002-0.022	0.1[(c)]
Endosulfan		3	0.054-0.067	2.0
Grapefruit (3 samples)	0			
Grapes (12 samples)	12			
Captan		3	0.1-1.4	50
Diazinon		1	0.18	0.75
Iprodione		2	0.67-0.84	60.0
Sulfur		9	1.2-82	- [(a)]
Kiwi (1 sample)	1			
Vinclozolin		1	1.2	10.0
Lettuce (2 samples)	0			
Nectarines (2 samples)	0			
Oranges (4 samples)	0			
Peaches (12 samples)	8			
Captan		6	0.006-2.2	50
Endosulfan		4	0.054-0.34	2.0
Iprodione		1	2.2	20.0
o-Phenylphenol		1	0.026	20
Permethrin		1	0.026	5.0
Propiconazole		1	0.43	1.0
Sulfur		1	0.36	- [(a)]
Pears (6 samples)	4			
Captan		1	0.15	25
Endosulfan		1	0.14	2.0
o-Phenylphenol		1	0.14	25.0
Permethrin		1	0.10	3.0
Phosmet		1	5.6	10
Peppers (5 samples)	2			
Endosulfan		1	0.05	2.0
Permethrin		2	0.013-0.026	1.0

Table 1. (Cont.) Summary of pesticides found in fresh fruits and vegetables sold in Connecticut, 2001.

Commodity (total samples) Pesticide	Samples with Residues	No. of Times Detected	Residue Range (ppm)	EPA Tolerance (ppm)
Pineapple (1 sample)	1			
Triademefon		1	0.32	3.0
Plums (2 samples)	1			
Sulfur		1	0.16	- [a]
Potatoes (11 samples)	3			
CIPC		2	0.54-0.62	50
Endosulfan		1	0.043	0.2
Raspberries (2 samples)	1			
Iprodione		1	0.92	2.0
Squash, summer (10 samples)	6			
Chlordane		1	0.002	0.1[c]
Chlorothalonil		3	0.01-0.11	5
DDE		1	0.02	0.1[c]
Endosulfan		5	0.014-0.2	2.0
Heptachlor epoxide		1	0.002	0.1[c]
Strawberries (28 samples)	23			
Bifenthrin		1	0.06	3.00
Captan		9	0.009-9	25
DCPA		3	0.05-0.20	2
Endosulfan		17	0.006-0.18	2.0
Fenhexamid		8	0.007-1.1	3.0
Folpet		1	0.64	25
Iprodione		1	0.62	15.0
Sulfur		1	0.84	- [a]
Vinclozolin		1	0.04	10
Sweet Potatoes (7 samples)	4			
DCNA		3	0.44-0.9	10
Diazinon		1	0.011	0.1
Tomatoes (31 samples)	10			
Captan		1	0.19	25
Chlorothalonil		7	0.01-0.56	5
Endosulfan		3	0.005-0.009	2.0
Permethrin		1	0.1	2
Miscellaneous (1 each)	0			
Cantaloupe, Eggplant, Mangoes, Mushrooms, Passionfruit, Rutabagas, Snow peas, Wax beans and Winter squash				

[a] Exempt from tolerance as per CFR180.2, GRAS
[b] Violative sample, no tolerance
[c] Action level as per FDA Compliance Policy Guidelines

Table 2. Summary of pesticides found in processed fruits and vegetables sold in Connecticut, 2001.

Commodity	Pesticide	Samples Analyzed	Samples with residues	No. of times detected	Residue range (ppm)
JUICES					
Apple Cider/Juice		49	0		
BABY FOOD					
Juice		7	0		
Miscellaneous Fruits/Vegetables		15	0		
FRUITS AND VEGETABLES*					
Carrots		2	0		
Eggplant		2	0		
Green Beans		1	0		
Mushrooms		1	0		
Mustard Greens		2	1		
	Permethrin			1	12[(a)]
Spinach		6	5		
	Permethrin			4	0.021-2.4
	DDE			3	0.008-0.022
Squash, winter		1	0		

*The green beans, eggplant, mustard greens and one of the spinach samples were canned. The carrots, mushrooms, squash and remaining five spinach samples had been washed and/or chopped and packaged.

[(a)] Violative sample, no tolerance

Table 3. 1990-2001 summary of all market-basket samples tested, including organic and processed food samples.

Year	Total Samples Tested	Samples With No Residues	Samples With Residues Within EPA Tolerances	Samples With Residues Over EPA Tolerances	Samples With Residues With No EPA Tolerances
1990	418	186	230	0	2
1991	285	190	94	0	1
1992	273	179	89	1	4
1993	441	305	128	3	5
1994	545	414	125	1	5
1995	444	307	129	0	8
1996	327	188	134	1(a)	4
1997	412	266	144	0	2
1998	180	115	63	0	2
1999	195	115	72	0	8
2000	145	90	54	1	0
2001	315	201	112	0	2
Total	3980	2556	1374	7	43

(a) Over FDA Action Level.

Table 4. Comparison of Connecticut Data with 1999 Data From California, FDA Domestic and Imported Samples, Florida and Portugal.

	No Residues (%)	Residues (%)	Violative (%)	Number of Samples
California (1999)	60	39	1	>7000
Connecticut (2001)	63	36	1	315
Connecticut (12 year average)	64	35	1	3980
FDA Domestic (1999)	60	39	1	3426
FDA Imported (1999)	65	32	3	6012
Florida (1999)	60	38	2	>3000
Portugal (1999)	61	34	5	757

Figure 1. Comparison of 2001 Connecticut Data with 1999 Data From California, FDA Domestic and Imported Samples, Florida and Portugal.