The Connecticut Agricultural Experiment Station, New Haven

Pesticide Residues in Produce Sold in Connecticut 2006 With a Comparison of Two Sample Preparation Methods

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INTRODUCTION

The Connecticut Agricultural Experiment Station (CAES) has analyzed food products for possible adulteration and published a bulletin on its findings for well over one hundred years (Krol, 2006). The food adulterants and the methods used for their detection have evolved over the course of time. However, the goal of this program continues to ensure that the food products offered for sale to the consumers in the state adhere to federal guidelines. The results of the pesticide monitoring study conducted in the Department of Analytical Chemistry have been published, at least in part, on an annual basis since 1963; and in a bulletin similar to the current one since 1988. In this present bulletin, we report our findings for 181 samples examined in 2006 employing laboratory methodology in use since 1988. We will refer to this method as the VegPrep method. Concurrently, the VegPrep work was compared with the new *Qu*ick, *E*asy, *Ch*eap, *E*ffective, *R*ugged, *S*afe (*QuEChERS*, pronounced "catchers") multi-residue methodology for pesticide residue analysis developed by USDA scientists (Anastassiades, 2003). The goal of the comparison was to ascertain what advantages, if any, the QuEChERS method would have for our laboratory.

In the United States (US), there are three government agencies that 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) for use and set pesticide residue tolerances if the use of a particular pesticide may result in residues on food (Reorganization plan No.3, 1970). The EPA relies upon the USDA and the FDA for Federal enforcement of food adulteration. 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 approach to pesticide residue monitoring, the model adopted as closely as possible for the market basket study described herein, involves collecting samples of individual lots of domestically produced and imported foods as close as possible to their point of entry into the distribution system; both the federal and state programs include the analysis of processed and raw foods for pesticide residues. When illegal pesticide residues are found, the FDA, or for samples grown in this State, The Department of Consumer Protection (DCP), can impose various sanctions, including seizure of the commodity or injunction. For those samples imported into the US, shipments will be stopped at the port of entry if they are 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 will be detained at the port of entry until analysis is complete (Schierow, 2004).

A residue tolerance is a commodity-specific, federally established upper limit to the amount of a chemical residue allowed on the individual food or feed product. A chemical residue includes the parent compound plus any degradates or metabolites. All substances intentionally applied to an agricultural crop must have a tolerance, or exemption from tolerance, established (40 e-CFR 180, 2007). 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 it is allowed. Tolerances are the only tool the EPA has under Federal law to control the quantity of pesticides on the food we consume.

To be able to enforce the EPA mandated tolerances, both the FDA and DCP must know the quantity and the type

of pesticide residues present in foodstuffs offered for sale. The DCP uses the laboratories of the Department of Analytical Chemistry at the CAES to perform analysis of foods sold within Connecticut for pesticide residues. This market basket survey concentrates on fresh produce grown in this state, but also includes fresh produce from other states and foreign countries and some processed food. The primary goal of this program is to determine if the amounts and types of pesticides found on fruits and vegetables are in accordance with the tolerances set by EPA. Violations of the law occur when pesticides are not used in accordance with label registration and are applied in excessive amounts, or when pesticides are accidentally or deliberately applied to crops on which they are not allowed.

There are currently 370 pesticide chemicals with tolerances for use in the US on over 1053 food commodities in twenty food groups. There are numerous other chemicals which have "exemptions from tolerances" or are "pesticide chemicals not requiring a tolerance or an exemption from a tolerance" (40 e-CFR 180, 2007). *There is no single method capable of simultaneously analyzing for all of these chemicals in all of the different food commodities.* While our VegPrep method of analysis provides detection of over 100 pesticides over a wide range of food, it was anticipated that the QuEChERS method used in this comparative study would provide expanded coverage for additional pesticide residues and additional sample matrices at enhanced levels of sensitivity.

METHODS

Sample Collection:

Samples of produce grown in Connecticut, other states, and foreign countries were collected at various Connecticut producers, retailers, and wholesale outlets by inspectors from the DCP. The samples collected were brought to our laboratory in New Haven for pesticide residue testing. These market basket samples were collected without prior knowledge of any pesticide application.

Sample Homogenization:

In most cases, each sample was prepared in its natural state as received, unwashed and unpeeled, but in all cases samples were processed according to the Pesticide Analytical Manual (PAM, 1994). Whole food samples were homogenized prior to extraction using a Hobart food Chopper or a commercial Waring® blender with an explosion proof motor. Liquid and coffee samples were mixed thoroughly prior to sub sampling for extraction. In all cases, a portion of each sample (*ca* 500 g) was retained and frozen in plastic Whirl-Pak® bags until analysis and reporting of the results were completed.

Sample Extraction:

A. VegPrep

The method described by Pylypiw (Pylypiw, 1993) was used in this work with minor modifications. A 50g subsample of homogenized material was weighed into a Waring® blender jar (1 L) and blended with 50 mL isopropyl alcohol and 100 mL petroleum ether (*ca* 5 min). After settling, the mixture was filtered through a plug of glass wool into a 500 mL separatory funnel to remove solids. Interfering co-extracted compounds and the isopropyl alcohol were removed from the petroleum ether extract by washing with water (3 x 200 mL). Saturated sodium sulfate (50 mL) was added to the first and the final wash to enhance partitioning and phase separation. After the final wash, the organic extract was collected in 40 mL glass vials containing anhydrous sodium sulfate (ca 10 g) which was used as a drying agent. *It should be noted that this extraction method results in a two-fold dilution factor of the original sample.*

B. QuEChERS

The QuEChERS method described by Anastassiades *et al***.** (Anastassiades, 2003) was modified for this work. A 15 g subsample of homogenized material was weighed into a 50 mL disposable polypropylene centrifuge tube. [U-ring]-$^{13}C_6$-Alachlor internal standard (60 µL of 10 ppm solution in toluene (i.e. 600 ng/15g)); prepared from material purchased from Cambridge Isotope Laboratories, anhydrous magnesium sulfate (6 g), anhydrous sodium acetate (1.5 g) and acetonitrile (15 mL) were added and the mixture was shaken on a Burrell Model 75 Wrist Action Shaker (ca 1h). The mixture was centrifuged using a Thermo IEC Centra GP6 Centrifuge at 3000 rpm for 10 min to separate the acetonitrile from the aqueous phase and solids. Acetonitrile (10 mL) was decanted into a 15 mL polypropylene Falcon® centrifuge tube containing magnesium sulfate (1.5 g), Primary and Secondary Amine (PSA) bonded silica (0.5 g) and toluene (2.0 mL). The mixture was shaken by hand (ca 5 min) and centrifuged at 3000 rpm for 10 min. Exactly 6.0 mL of the extract was added to a concentrator tube and blown down to just under 1 mL (but not to dryness) under a stream of nitrogen at 50 ºC. The concentrated material was brought up to a final volume of 1 mL with toluene. *It should be noted that this extraction method results in a five-fold concentration of the original sample.*

Instrumental Analysis:

A. VegPrep

Samples prepared by the VegPrep method were analyzed using an Agilent 6890 plus Gas Chromatograph (GC) equipped with: dual 7683 series injectors and a 7683 autosampler (collectively known as an Automatic Liquid Sampler (ALS)); Agilent model number G2397A micro Electron Capture Detector (μECD) and a 5973 Mass Spectral Detector (MSD); a Programmable Temperature Vaporization (PTV) on the front inlet leading to the MSD and a Merlin MicroSeal® system on the rear inlet leading to the ECD; dual Supelco® MDN-12 fused silica capillary columns (30 m x 250 μm x 0.25 μm). Injections were made simultaneously onto both columns, and all data were collected and analyzed using MSD Productivity Chemstation Software version B.02.00.

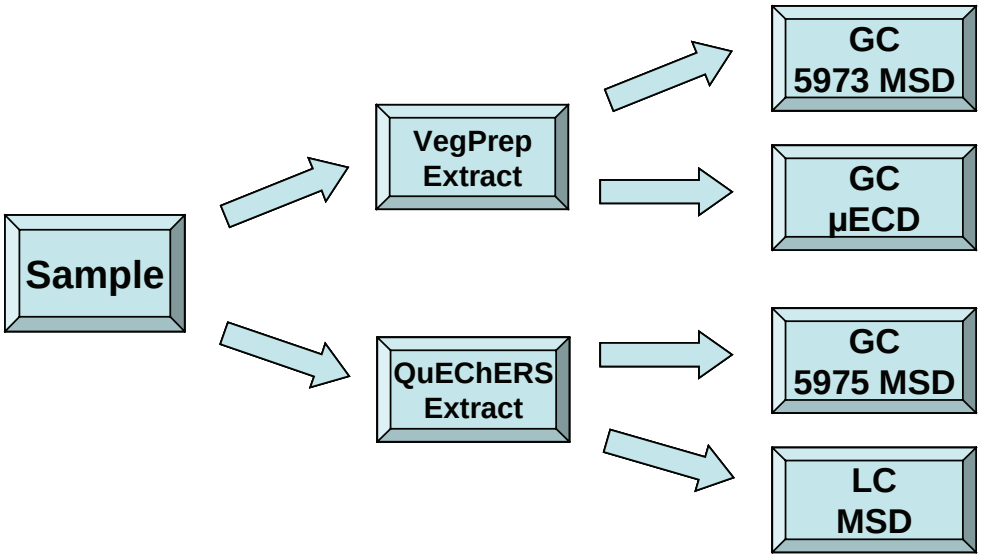
B. QuEChERS

Samples prepared by the QuEChERS method were analyzed by GC and by Liquid Chromatography (LC). For the GC analysis, an Agilent 6890N GC equipped with a 7683 series ALS and 5975 MSD was used. The inlet used a Merlin MicroSeal® system with injections made onto a J&W Scientific DB-5MS+DG (30 m x 250 μm x 0.25 μm) column. Data were collected and analyzed using MSD Chemstation Software version D.02.00.275. The LC analyses were made using an Agilent 1100 High Pressure Liquid Chromatograph (HPLC) and Zorbax® SB-C18 (2.1 mm x 150 mm, 5μ) column with eluant flowing to a Thermo-Electron LTQ ion trap mass spectrometer. Data were collected and analyzed using Xcalibur® software version 2.0.

RESULTS AND DISCUSSION

In 2006, our laboratory conducted a comparative study of our longstanding VegPrep method with the QuEChERS method used for the extraction of pesticide residue from food matrices. The 181 samples of fresh (140; 77.3%) and processed (41; 22.7%) food[1] were each individually extracted using both the VegPrep method and the QuEChERS method resulting in 362 extracts. The VegPrep extracts were *ten times* more dilute than the QuEChERS extracts owing to the extraction protocols. The VegPrep extracts were analyzed by GC simultaneously employing both micro-Electron Capture (μEC) and 5973 Mass Spectral (MS) detection utilizing older (2000) instrumentation. The QuEChERS extracts were analyzed by GC with newer (2005), more sensitive 5975 MS detection and by new (2005) LC/MS. The samples were extracted and analyzed as outlined in the flowchart shown in Figure 1.

Figure 1: Flowchart of 2006 Sample Extract and Analysis



[1] The implementation of the Food Quality Protection Act (FQPA, 1996) provides a single safety standard for pesticide residue levels in raw agricultural commodities and processed foods. In the present work, no distinction is made between sample types in any statistical analysis. Thus, for example, a residue reported on fresh tomatoes is equivalent to that of a residue found in a jar of pasta sauce.

The survey results obtained by the VegPrep method are comparable to those in previous years of our study using this method (see Tables 4 & 5). Of the 181 samples analyzed by this protocol, 98 (54.1%) of the samples contained no pesticide residues; 79 (43.7%) contained non-violative residues; 4 (2.2%) contained violative residues (Table 4). A total of 133 different pesticide residues were found on the 83 samples containing pesticide residues. By comparison, in 2005 when a total of 163 samples were analyzed, 93 (57.1%) of the samples contained no pesticide residues; 67 (41.1%) contained non-violative residues; 3 (1.9%) contained violative residues (Table 5). A total of 109 different pesticide residues were found on the 70 samples containing pesticide residues.

By contrast, when the same 181 samples were extracted by the QuEChERS method and the extract analyzed by both GC and LC, 73 (40.3%) of the samples were found to contain no pesticide residues. Of the remaining 108 samples, which contained 180 different pesticide residues, 89 (49.2%) contained non-violative residues and 19 (10.5%) contained violative residues. Of these 180 residues, 111 were detected by GC and 138 were detected by LC with 69 residues confirmed by both instrumental methods of analysis.

When the results of the two protocols are taken together, it was found that only 59 (32.6%) of the 181 samples examined contained no pesticide residues. The remaining 122 samples contained residues of 34 different pesticides; 102 (56.3%) of those samples contained non-violative residues; 20 (11.1%) contained violative residues. Table 1 shows the frequency that each of the 34 pesticides detected was found on individual commodities. Table 2 provides a detailed breakdown of pesticide residues observed by instrumental method for the four quarters of 2006. The data in Table 2 clearly show that the determination of pesticide residues is not only instrument specific, but also method specific with respect to the extraction of some of the pesticide residues.

The combined results of the 2006 survey contrast with those obtained in our studies since 1990 (Table 5) and the most recently published 2003 pesticide residue monitoring report published by the FDA (FDA, 2003) which are summarized and compared to our data in Table 3. This is due in large part to the introduction of the QuEChERS method, and in part to combining the results of two protocols. Note that the values provided in Tables 3 and 5 are the sum of the VegPrep and QuEChERS protocols.

Sixteen (8.8%) of the 181 samples analyzed in 2006 were labeled as certified organic produce[2]. Of these sixteen samples, ten were fresh and six were processed. Twelve of the samples were domestically grown, two were grown outside the US and two were of unknown origin. Six of the domestic samples were grown in Connecticut. The organically labeled produce consisted of bananas (3), spinach (2), and one sample each of apples, snap beans, cabbage, cherries, cucumbers, greens, kale, sweet potato, strawberries, summer squash and tomatoes. Of these certified organic samples 4 (25%) were found to contain pesticide residues. Three fresh produce samples from Connecticut were found to contain pesticide residues; a sample of cucumbers was found to contain 0.04 ppm dieldrin; a sample of kale was found to contain 0.02 ppm carbaryl; a sample of sweet potatoes was found to contain 0.003 ppm chlorothalonil. A sample of chopped, packaged spinach from California was found to contain 0.01 ppm DDE a breakdown product of DDT.

In 2006, CAES reported 20 no tolerance pesticide residue violations, far surpassing any previous survey. This is likely a result of several factors. The QuEChERS sample extract provides a ten fold increase (one order of magnitude) in sensitivity for pesticide residues. The use of the LC/MS in the screening process allows for the analysis of new classes of pesticides that can not be detected using GC. This instrument is also extremely sensitive and has the capability of detecting pesticides in the parts per trillion (ppt). One part per trillion is one second in 31,708 years.

Seven pesticides accounted for all 20 of these violations. The herbicide atrazine accounted for nine violations (0.0002 - 0.015 ppm); the fungicide chlorothalonil, four (0.02 – 0.8 ppm); the insecticide chlorpyrifos (0.003 – 0.017 ppm), three; the insecticide fenpropathrin, one (0.019 ppm); and the fungicides diphenylamine (0.01 ppm), fenbuconazole (0.002 ppm) and myclobutanil (0.007 ppm) for one each. The commodities on which

[2] Produce bearing the 'Organic' label must comply with the with the USDA National Organic Program guidelines. For more information on this topic the reader is referred to The National Organic Program Homepage: http://www.ams.usda.gov/nop/indexIE.htm.

these were found are shown in Table 1.
All of the atrazine violations were detected through the QuEChERS protocol by LC/MS. In most cases (8) atrazine was detected on crops which are in contact with soil (lettuce, spinach, etc.) leading to a hypothesis that the leafy green vegetable might uptake and concentrate this herbicide. In one case, however, atrazine was found on blueberries. An important corollary of these findings emerged in early 2007 when, largely as a result of these findings, the EPA issued Action Levels for atrazine on several crops. Atrazine can bind and persist in surface soil (Blume, E *et.al.*, 2004). It is thought that soil dust is responsible for the indirect transfer of atrazine to the crops on which it is found. The EPA has chosen to declare Action Levels for residues of atrazine due to its environmental persistence (Hrdy, D., 2007).

Seven of the violations reported are for Connecticut grown produce. One sample of blueberries and one sample of lettuce grown in Connecticut contained atrazine. The lettuce grower indicated that atrazine was last applied to the field three years' ago. One sample each of peaches containing fenpropathrin, apples containing fenbuconazole, and pears containing diphenylamine grown in Connecticut were found to be no tolerance violations meaning that these pesticides are not allowed on these commodities. It is interesting to note that allowable residues of the pesticides in question were also found in other types of produce obtained at the same time from the growers in question. One sample of lettuce was found to contain chlorpyrifos, and one sample of sweet potatoes was found to contain myclobutanil. In all these cases, the growers were notified of their respective violations by the DCP.

Four samples of peas (snow or snap) from two separate growers in Guatemala were found to contain residues of chlorothalonil. Results of these analyses were forwarded to the DCP which in turn forwarded them to the FDA for enforcement. These samples were collected in the last weeks of December of 2006. It should be noted that two additional imported samples of peas from Guatemala received in our laboratories for testing in January 2007 also contained residues of chlorothalonil. These samples are not included in the results of this bulletin.

CONCLUSIONS

In conclusion, when the data from the VegPrep protocol are taken alone the percentage of samples found to contain no pesticide residues, 54.1 %, was similar to that in the previous years of our market basket survey. In comparison, the QuEChERS protocol found fewer samples, 40.3%, with NO pesticide residues. Of the thirty-four pesticides found, twenty-four were identified concurrently by both methods, with six being exclusively identified by QuEChERS and four by the VegPrep protocols. The average pesticide residue found using the VegPrep method was 0.577 ppm, yet was 0.162 ppm using the QuEChERS method. The minimum pesticide residue found with the VegPrep method was 0.001 ppm yet was 0.0002 ppm using the QuEChERS method. Based upon the results of this comparative study, the QuEChERS protocol has been adopted in our laboratories as the method of choice for future market basket survey work.

There were a total of 20 violative samples in 2006, more than in any other year in which the VegPrep method was used alone. It can be concluded that this is in part due to the fact that each sample was analyzed effectively in duplicate, using two separate extraction protocols and newer and more sensitive analytical instrumentation for the analysis of pesticide residues in these extracts.

Organic produce is not pesticide free. Analysis of 16 organically grown samples of produce showed that four samples (25%) contained pesticide residues. In all these cases, the residues found were within US EPA tolerance. Comparatively in 2005 twenty percent (2) of the certified organic samples (10) were found to contain pesticide residues.

The results of all analyses have been forwarded to DCP for regulatory enforcement purposes. In the case of out of state violative samples the DCP has forwarded the analytical results to the FDA.

A breakdown of the results of our survey into fruit and vegetable categories allows a direct comparison of our results to those obtained from the FDA survey. The results contained herein in combination with the data obtained by the FDA support the fact that the vast majority of the produce offered for sale contain either no pesticides residues, or residues that are within the guidelines of US Federal Law.

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Table 1: Commodities Studied and Frequency of Pesticides Found

	Total Number of Samples	Acephate	Acetamiprid	Atrazine & Metabolites	Bifenthrin	Boscalid	Captan	Carbaryl	Chlordane	Chlorothalonil & Metabolites	Chlorpyrifos	CIPC	Cyhalothrin, Lambda	Cypermethrin	Cyprodinil	DDT & Metabolites	Dieldrin	Dimethomorph	Diphenylamine	Endosulfan	Fenhexamid	Fenbuconazole	Fenpropathrin	Fenvalerate	Fludioxinil	Imazalil	Iprodione	Malathion	Methomyl	Metolachlor	Myclobutanil	Permethrin	Phosmet	Sulfur	Trifloxystrobin
Apples	**19**		2			5	10	4											1	1		**1**	4								2		14		1
Arugala	**1**			**1**																														
Asparagus	**2**																																	
Bananas	**6**																								1									
Beans	**7**	1						1		3										2														
Beets	**1**						1																											
Blueberries	**12**			**1**		1	3				1									2	2			1				1	1			2		
Brocolli	**1**																																1	
Cabbage	**1**																																	
Cantaloupe	**1**							1												1														
Cherries	**2**					1	1																											
Cider	**5**					4		2											1				1									3		
Coffee	**3**																																	
Corn	**4**							1																										
Cucumbers	**7**									1						1	2			1														
Eggplant	**3**																																	
Fruit Cocktail	**3**							2							2																			
Grapes	**2**																												1				1	
Greens	**1**																																	
Kale	**1**							1																										
Leeks	**1**																																	
Lettuce	**5**			**1**							1		1							2														
Mangoes	**1**																																	
Nectarines	**2**										1											1			1							1	1	
Peaches	**8**						4				1		2		3					5	1	6	1		1							3	1	
Pears	**5**									1			1		1				1	2												5		
Peas	**7**									4										1														
Peppers	**9**	1					1																											
Plums	**1**										1														1									
Potatoes**	**10**										1	4				1	1			3										1				
Raspberries	**1**							1													1					1								
Salad Mix	**1**			**1**																														
Spinach	**11**			**5**				1			1			1		1																3		
Squash***	**11**								1		1					1	5			3											1				
Strawberries	**18**				3	1	2	1			1				12					7	2		6					1		1			1	
Tomatoes	**8**				1			1										1		2														
Sum Totals	181	2	2	9	4	12	22	16	1	9	8	4	4	1	18	4	8	1	3	32	6	8	12	1	3	1	1	2	2	1	4	3	28	5	1
Total Pesticides	238	****Includes 1 sweet potato sample containing chlorpyrifos; a no tolerance violation**																																	
		*****Includes 6 Summer and 5 Winter squash; 1 winter squash containing myclobutanil; a no tolerance violation**																																	

Table 2: Pesticide Residues Found by Quarter 2006

	1st Quarter (Jan - Mar)				2nd Quarter (Apr - Jun)				3rd Quarter (Jul- Sept)				4th Quarter (Oct-Dec)				
Pesticide	1st Q	Detected By			2nd Q	Detected By			3rd Q	Detected By			4th Q	Detected By			**Yearly**
	Totals	Veg Prep	5975	LTQ	Totals	Veg Prep	5975	LTQ	Totals	Veg Prep	5975	LTQ	Totals	Veg Prep	5975	LTQ	**Total**
Acephate	1			1					1			1					**2**
Acetamiprid													2			2	**2**
Atrazine & Metabolites	2 **(2)**			2 (2)	6 **(6)**			6 (6)	1 **(1)**			1 (1)					**9**
Bifenthrin					4	4											**4**
Boscalid					2	2		2	1	1		1	9		5	9	**12**
Captan	1	1	1		1		1		12	9	9		8	7	7		**22**
Carbaryl					6			6	4		1	4	7		3	7	**16**
Chlordane													1	1	1		**1**
Chlorothalonil & Metabolites	1	1	1						2	1	2		6 **(4)**	2 (1)	5 (3)	5 (2)	**9**
Chlorpyrifos					6 **(2)**	3 (2)		6 (2)	2 **(1)**			2 (1)					**8**
CIPC	3	3	3	2	1	1	1	1									**4**
Cyhalothrin, lambda-					1	1			2	2	1		1	1		1	**4**
Cypermethrin					1	1											**1**
Cyprodinil	2	1	2	2	12	8	1	12	4		2	4					**18**
DDT & Metabolites					1	1	1		1	1			2	2	1		**4**
Dieldrin									5	5	3	1	3	3	1		**8**
Dimethomorph					1			1									**1**
Diphenylamine													3 **(1)**	1	3 (1)	2 (1)	**3**
Endosulfan	4	4	2		10	10			9	9	2		9	6	3		**32**
Fenhexamid	1	1	1	1	1	1		1	3		2	2	1	1	1	1	**6**
Fenbuconazole									8 **(1)**	4	8 (1)	8 (1)					**8**
Fenpropathrin					6	6	1	1	2	2	1		4 **(1)**	3 (1)	3	4	**12**
Fenvalerate					1	1											**1**
Fludioxinil					3	3		3									**3**
Imazalil					1	1	1	1									**1**
Iprodione													1	1	1	1	**1**
Malathion					2	1		2									**2**
Methomyl					1			1	1			1					**2**
Metolachlor	1	1	1	1													**1**
Myclobutanil					1	1							3 **(1)**		3 (1)	3 (1)	**4**
Permethrin					3	3											**3**
Phosmet									11	4	11	11	17	1	14	16	**28**
Sulfur					3	3			2	2							**5**
Trifloxystrobin									1	1	1	1					**1**
Sum totals	**16**	12	11	8	**73**	51	6	42	**72**	41	43	37	**77**	29	51	51	**238**

Violative Residues Shown Red in Parenthesis

Table 3: Comparison of 2003 FDA Data with 2003-2006 Connecticut Data

2003 FDA Summary Data	Total Samples	No Residues	Non-Violative Residues	Violative Residues	Tolerance Over	Tolerance No
FDA Domestic Fresh & Processed Fruits	**813**	**395** (49.0%)	**400** (49.0%)	**18** (2.0%)	0	18
FDA Domestic Fresh & Processed Vegetables	**1132**	**783** (69.1%)	**327** (29.0%)	**22** (1.9%)	1	21
FDA Fresh & Processed Imported Fruits	**1537**	**977** (63.6%)	**478** (31.1%)	**82** (5.3%)	3	79
FDA Fresh & Processed Imported Vegetables	**2494**	**1808** (72.5%)	**519** (20.8%)	**167** (6.7%)	15	152
2003 Connecticut Summary Data[1]						
CT Fresh & Processed Fruit	**76**	**50** (65.8%)	**26** (34.2%)	**0** (0.0%)	0	0
CT Fresh & Processed Vegetables	**57**	**36** (63.2%)	**17** (29.8%)	**4** (7.0%)	0	4
Domestic Fresh & Processed Fruit (incl. CT)	**129**	**81** (62.8%)	**46** (35.7%)	**2** (1.5%)	1	1
Domestic Fresh & Processed Vegetables (incl. CT)	**136**	**79** (58.1%)	**32** (23.5%)	**6 (**4.4%)	0	6
Imported Fresh & Processed Fruit	**32**	**20** (62.5%)	**12** (37.5%)	**0** (0.0%)	0	0
Imported Fresh & Processed Vegetables	**14**	**11** (78.6%)	**3** (21.4%)	**0** (0.0%)	0	0
2004 Connecticut Summary						
CT Fresh & Processed Fruit	**69**	**35** (50.7%)	**32** (46.4%)	**2** (2.9%)	0	2
CT Fresh & Processed Vegetables	**54**	**37** (68.5%)	**17** (31.5%)	**0** (0.0%)	0	0
Domestic Fresh & Processed Fruit (incl. CT)	**99**	**54** (54.6%)	**43** (43.4%)	**2** (2.0%)	0	2
Domestic Fresh & Processed Vegetables (incl. CT)	**75**	**54** (72.0%)	**21** (28.0%)	**0** (0.0%)	0	0
Imported Fresh & Processed Fruit	**10**	**7** (70.0%)	**3** (30.0%)	**0** (0.0%)	0	0
Imported Fresh & Processed Vegetables	**13**	**7** (53.8%)	**5** (38.5%)	**1** (7.7%)	0	1
2005 Connecticut Summary[2]						
CT Fresh & Processed Fruit	**54**	**22** (40.7%)	**30** (55.6%)	**2** (3.7%)	0	2
CT Fresh & Processed Vegetables	**32**	**21** (65.6%)	**10** (31.3%)	**1** (2.9%)	0	1
Domestic Fresh & Processed Fruit (incl. CT)	**79**	**38** (48.1%)	**39** (49.4%)	**2** (2.5%)	0	2
Domestic Fresh & Processed Vegetables (incl. CT)	**51**	**31** (60.8%)	**19** (37.3%)	**1** (1.9%)	0	1
Imported Fresh & Processed Fruit	**12**	**7** (58.3%)	**5** (41.7%)	**0** (0.0%)	0	0
Imported Fresh & Processed Vegetables	**8**	**6** (75.0%)	**2** (25.0%)	**0** (0.0%)	0	0
2006 Connecticut Summary[3]						
CT Fresh & Processed Fruit	**62**	**3** (4.8%)	**55** (88.7%)	**4** (6.5%)	0	4
CT Fresh & Processed Vegetables	**50**	**26** (52.0%)	**20** (40.0%)	**4** (8.0%)	0	4
Domestic Fresh & Processed Fruit (incl. CT)	**73**	**6** (8.2%)	**63** (86.3%)	**4** (5.5%)	0	4
Domestic Fresh & Processed Vegetables (incl. CT)	**75**	**35** (46.7%)	**31** (41.3%)	**9** (12%)	0	9
Imported Fresh & Processed Fruit	**10**	**7** (70.0%)	**3** (30.0%)	**0** (0.0%)	0	0
Imported Fresh & Processed Vegetables	**10**	**6** (60.0%)	**0** (0.0%)	**4** (40.0%)	0	4

[1] Does not include data for 3 samples of unknown origin.
[2] Does not include data for 13 samples of unknown origin.
[3] Does not include data for 13 samples of unknown origin of which 3 were no tolerance violations

Table 4: Summary by Instrumental Method:

	VegPrep	QuEChERS 5975*	QuEChERS LTQ	Combined QuEChERS	Total
Without Residues	98 (54.1)	117 (64.6)	86 (47.5)	73 (40.3)	59 (32.6)
Non Violative Residues	79 (43.7)	58 (32.1)	76 (42.0)	89 (49.2)	102 (56.3)
Violative Residues	4 (2.2)	6 (3.3)	19 (10.5)	19 (10.5)	20 (11.1)
Totals	**181**	**181**	**181**	**181**	**181**

Reprted as Number of Samples (Percent of Total)

*No Data Collected on this Instrument in the 2nd Q

Table 5: Summary of All Market Basket Samples, Including Organic and Processed Food 1990 - 2006.

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 Tolerance
1990	418	186 (44.5)	230	0	2
1991	285	190 (66.7)	94	0	1
1992	273	179 (65.6)	89	1	4
1993	443	305 (68.8)	128	3	7
1994[d]	545	414 (76.0)	125	1	5
1995	444	307 (69.1)	129	0	8
1996	327	188 (57.5)	134	1[a]	4
1997	412	266 (64.6)	144	0	2
1998	180	115 (63.9)	63	0	2
1999[e]	195	115 (59.0)	72	0	8
2000	145	90 (62.1)	54	1	0
2001	315	201 (63.8)	112	0	2
2002	206	137 (66.5)	68[b]	0	1
2003	298	195 (65.4)	95	1	7[c]
2004	197	122 (61.9)	71	1	3
2005	163	93 (57.1)	67	0	3
2006[f]	181	59 (32.6)	102	0	20
Total	**5027**	**3162**	**1777**	**9**	**79**

(a) Over FDA action level
(b) Two samples listed as organic, but below 5% of the EPA tolerance
(c) Includes two “action level” violations, DDE is not allowed on broccoli rabe
(d) 1994 MSD confirmation of pesticide residues began
(e) 1999 Began analyzing all samples by ECD and MSD
(f) 2006 Began QuEChERS GC- and LC/ MSD analysis of all samples

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