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Pesticide Residues
in Produce Sold
in Connecticut
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INTRODUCTION

The Connecticut Agricultural Experiment Station (CAES) first reported its findings on pesticide spray residues in food products almost eight decades ago (Bailey, 1932). Beginning with the inception of our market basket study in 1963, Connecticut is the only state in New England that has continuously monitored its food supply for pesticide residues through work done in cooperation with the State of Connecticut Department of Consumer Protection (DCP). Food commodities included in all these studies were grown not only in Connecticut, but also in other parts of the world. The results of the pesticide monitoring studies have been published, at least in part, on an annual basis since 1963 (Krol, 2006). Since 1988 CAES has published annual bulletins dedicated solely to the analysis of pesticide residues in foods included in this ongoing study. The food adulterants and the methods used for their detection have evolved over the course of time. The goal of this program, however, continues to ensure that the food products offered for sale to the consumers in the state adhere to federal guidelines in their production. We herein report the findings of pesticide residues in produce sold in Connecticut in 2007.

In the United States (US), there are three federal 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 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. In Connecticut, random samples of food are obtained from local markets and roadside stands where they are offered for sale to the consumer. 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 DCP can impose various sanctions including seizure of the commodity or injunction. For those samples imported into the US, shipments may 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 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 (Vida infra). All substances intentionally applied to an agricultural crop must have a tolerance, or exemption from tolerance, established (40 e-CFR 180, 2008). It is a violation of Federal law to intentionally apply a pesticide chemical to a crop not listed on the original pesticide container label. 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, as well as processed food. The primary goal of this program is to determine if the amounts and types of pesticides found on fruits and vegetables adhere to 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 (over tolerance), or when pesticides are accidentally or deliberately applied to crops on which they are not allowed (no tolerance). In all cases the results of the lab findings at the CAES are forwarded to the DCP. For violations found on crops grown within this state, the DCP notifies both the grower and the Connecticut Department of Environmental Protection (DEP) of the results. The DEP performs an audit of the grower's records to ensure proper pesticide use. The DCP may, at its discretion recall or destroy the violative commodity and/or may request re-testing of the sample.

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. In nearly all cases, 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 powdered samples were mixed thoroughly prior to sub-sampling for extraction. In all cases, a portion of each sample (ca 500 g) was retained in either a refrigerated or frozen state in its original packaging or in plastic Whirl-Pak® bags until analysis and reporting of the results were completed.

Sample Extraction:

The Quick, Easy, Cheap, Effective, Rugged, Safe (QuEChERS; pronounced "catchers") multi-residue methodology described by Anastassiades et al. (Anastassiades, 2003) was modified for this work. A 15 g sub sample of homogenized material was weighed into a 50 mL disposable polypropylene centrifuge tube. [U-ring]-$^{13}C_6$-Alachlor Internal Standard (IS) (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) (collectively referred to as 'salts') 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 1.0 mL with toluene. It should be noted that this extraction method results in a five-fold concentration of the original sample. In the case of honey, dried powders, wheat and rice glutens etc, smaller sample sizes (3-5 g) were used, and distilled deionized water added to give a final sample size of 15 g prior to the introduction of the IS, salts and acetonitrile.

Instrumental Analysis:

Samples extracted by the QuEChERS method were analyzed by Gas Chromatography (GC) and Liquid Chromatography (LC). For the GC analysis, an Agilent 6890 plus 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 (MS) Detector; a Programmable Temperature Vaporization (PTV) on the front inlet leading to the MS, and a Merlin MicroSeal® system on the rear inlet leading to the µECD; dual J&W Scientific DB-5MS+DG (30 m x 250 µm x 0.25 µm) columns. Injections were made simultaneously onto both columns, and all data were collected and analyzed using MSD Productivity Chemstation Software version B.02.00. The LC analyses were made using an Agilent 1100 High Pressure Liquid Chromatograph (HPLC) equipped with a Zorbax® SB-C18 (2.1 mm x 150 mm, 5µ) column; 6µL injection volume; flow rate 0.25 mL/min; gradient flow 87.5% A (H2O/0.1N HCOOH) to B (100% MeOH/0.1N HCOOH) over 20 min; hold 100% B for 10 min. The column eluant was interfaced 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 we performed a comparative study of our longstanding VegPrep methodology with the QuEChERS extraction method, followed by gas and liquid chromatographic analyses (Krol, 2007). As a result of this study, we have adopted the QuEChERS protocol for extracting pesticide residues from produce samples. The QuEChERS protocol has gained widespread acceptance and has become an AOAC accredited method for the analysis of pesticide residues (AOAC, 2007; Method 2007.01). To gain this accreditation, a study was conducted in which twenty representative pesticides were fortified in three different matrices at three duplicate levels, unknown to collaborators, at 10 – 1000 ng/g. Thirteen (13) laboratories located in seven (7) countries provided results for this study (Lehotay, 2007).

It is noteworthy that the QuEChERS extraction method is applicable to low moisture and high sugar content samples. Consequently, several samples of honey were analyzed in response to a consumer complaint, and ‘grain’ samples were analyzed as part of a targeted protein surveillance study in 2007.

In 2007, five honey samples were analyzed using the QuEChERS method. The method was modified slightly, in that three (3) grams of honey was dissolved in 12 mL of water prior to the addition of the IS and salts. The honey samples were all from the US, and originated in Connecticut (2), Pennsylvania (2) and Iowa (1). All the samples were found to contain residues of the acaricides coumaphos (0.001 - 0.008 ppm; avg. 0.0034 ppm) and fluvalinate (0.001 - 0.003 ppm; avg. 0.002 ppm). These acaricides are impregnated in strips which are hung in bee hives to control, among other things, varroa mites.

In 2007, fifteen (15) samples consisting of high protein corn, soy, rice, and wheat flours, meals, gluten and protein drinks were analyzed using a modified QuEChERS extraction protocol. Three (3) grams of sample were suspended in 12 mL of water prior to adding the IS and salts, as with the honey samples. These samples were all processed foods of unknown specific origin; however all the products were manufactured in the US. Two (2) of the rice flour samples were organic. None of the samples examined was found to contain pesticide residues. Unpublished work carried out concurrently in our laboratories demonstrated that $^{13}C_6$-Alachlor IS added into the samples provided an average recovery of 98.0 %. Additionally, the addition of twelve (12) representative pesticides at either 600 or 3000 ng/15g to duplicate samples provided recoveries of between 82 - 115%.

It is notable that field-incurred pesticides were recovered in the honey samples, and that added pesticides could be recovered from the ‘grain’ samples (such as wheat and rice) employing the QuEChERS extraction methodology.

Throughout 2007, we have concentrated on building mass spectral libraries of pesticide active ingredients (AIs) on the GC and especially on the LC. This was achieved by obtaining a large number of AI pesticide chemical standards from the EPA pesticide chemical repository, and obtaining mass spectra of these AIs using LC and GC instrumental conditions similar to those used for the analysis of unknown samples. Unknowns in the QuEChERS extracts were compared to these libraries for the identification of pesticide residues present in the sample. In late August of 2007 over 150 pesticide AIs were added to the LC library, leading to an increased number of residues detected in Q4 of 2007 (See Table 2). By using the QuEChERS sample extraction protocol, analyzing the resulting extracts by both GC and LC, and building these new libraries, we have realized a tremendous increase in the number of pesticide residues found in approximately the same number of samples since 2005.

Figure 1: Number of Pesticide Residues found in Samples 2005 – 2007.

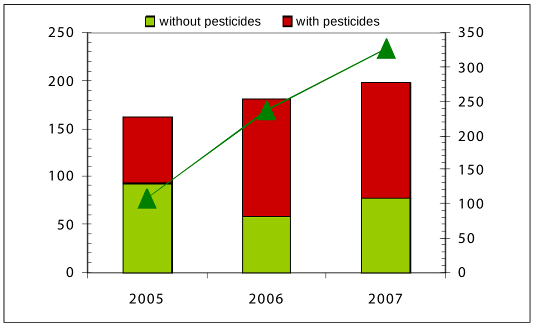

Figure 1 graphically depicts the improvements made to our pesticide residue program since 2005. In 2005, 163 samples were extracted using VegPrep methodology which had been in place since the early 1990s (Krol, 2007). The samples were analyzed by GC with µECD and MS detection. A total of 109 pesticide residues were found in 70 (42.9%) of the samples. In samples containing residues, the average residue value was 0.960 ppm, and the average number of pesticides found on a sample was 1.56. In 2006 the QuEChERS sample extraction protocol was introduced and compared to the VegPrep method resulting in duplicate sample extraction (Krol, 2007). Samples arising from the QuEChERS extracts were analyzed by both GC and LC with MS detection. Samples arising from the VegPrep extract were analyzed by GC with µECD and MS detection. A total of 181 samples (362 extracts) were analyzed resulting in 238 pesticide residues being found in 122 (67.4%) of the samples. In those samples containing residues, the average residue value was 0.221 ppm, and the average number of pesticides found on a sample increased to 1.95. In 2007, all samples were extracted using only the QuEChERS method, and analyzed by LC with MS detection and by GC with µECD and MS detection. A total of 198 samples were analyzed resulting in the detection of 327 residues in 120 (60.6%) of the samples. The average residue found was 0.163 ppm, and the average number of pesticide residues found on each sample was 2.62 in 2007. These values changed in Q4 to 0.093 ppm and 3.21 respectively when the LC library was expanded. Since 2005, the average residue value has decreased by a factor of 10, and the number of pesticides residues detected has more than doubled! In 2006 the impact of employing the QuEChERS method combined with LC/MS analysis resulted in finding sixteen additional violative residues that were not detected by the VegPrep method, and eleven that could only be found employing LC/MS[1] .

In 2007, 198 samples of fresh (118; 59.6%) and processed (80; 40.4%) fruits (100), vegetables (87) and other (11 total: honey (5); grain (6)) samples were analyzed for pesticide residues (Tables 1&2)[2] . A total of 45 different pesticide active ingredients were detected and quantitated. Table 1 provides a breakdown of the commodities analyzed in 2007. It includes the number of times each commodity was tested, the pesticides found on each commodity, and the frequency that pesticides were found on each particular commodity. Table 2 summarizes the pesticides detected by quarter, the frequency of their detection and the instrument(s) by which they were detected. Of the 198 samples analyzed, 78 (39.4%) contained no detectable pesticide residues. The remaining 120 (60.6%) samples contained 327 pesticide residues. Of these 120 samples, six samples contained residues which had no tolerance on the commodities to which they were applied and were therefore violative. Details of the violative samples are provided individually below. The frequency of pesticide residues found and the commodities on which they were found is shown in Table 1&2 with the violative residues shown in **red bold text**. A summary comparison of the 2007 findings is made with data from 1990 - 2006 in Table 3. The implementation of modern methodology in our analysis since 2006 becomes readily apparent by comparing the 'Samples with NO Residues' and 'Average Pesticide Residue (ppm)' columns for 2006 - 2007 with data obtained in previous years of our study.

The six samples which contained illegal residues comprised three pea (2 fresh; 1 processed) samples grown outside the US, one sample each of processed black currants and fresh plums grown in Connecticut, and one sample of processed spinach grown in the US outside Connecticut. Two of the three pea samples were found to contain residues of the fungicide chlorothalonil (0.036 & 0.196 ppm). These fresh snap pea samples were analyzed in January of 2007 and were from Guatemala. In December of 2006 four samples of peas (snow or snap) from two separate growers in Guatemala were found to contain residues of chlorothalonil (0.018 - 0.752 ppm) which were reported in the 2006 Bulletin (Krol, 2007). The third, processed, sweet pea sample of unknown origin was found to contain residues of carbaryl (0.516 ppm). The results of all these analyses were forwarded to the DCP, and in turn forwarded to the district office of the FDA. These results led the FDA to place peas from Guatemala on automatic detention without physical examination status. This requires that samples entering the US be tested for pesticide residues prior to their release into the US marketplace. It should be noted that this ruling did not apply to all companies operating in Guatemala.

A sample of black currant juice from Connecticut was found to contain residues of the insecticide carbaryl (0.006 ppm). The grower indicated to DCP that carbaryl had not been applied to the 2006 crop of black currant used in the production of this juice. The grower, in cooperation with the DCP, submitted samples of water, sugar, 2006 black currant concentrate (from the 9 remaining barrels) and black currants from the 2007 growing season for analysis. The concentrate, which had not yet been diluted to make juice, was the only sample found to contain carbaryl (0.266 ppm). It is interesting to note that black currant concentrate is diluted by a factor of 40 to produce juice (0.266 / 40 = 0.0066). The current FDA limit of detection for carbaryl is 0.010 ppm (Krol, 2008 personal FDA communication). The lower limit of detection reproducibly achieved at the CAES underscores the effectiveness of the QuEChERS extraction protocol. This protocol has not yet been implemented at the Federal level. Based upon recommendations from the FDA and the Connecticut Department of Public Health, no enforcement action was taken by the DCP. The remaining black currant concentrate was allowed to be diluted to juice and offered for sale in the US marketplace.

A sample of plums grown in Connecticut was found to contain illegal residues of permethrin (0.085 ppm). Three other pesticides, boscalid (0.177 ppm), captan (0.260 ppm) and endosulfan (0.073 ppm) were also found on this sample. In a sample of peaches obtained concurrently with the plums from the same grower, residues of boscalid (0.21 ppm), captan (0.491 ppm), endosulfan (0.490 ppm) and permethrin (0.099 ppm) were found. The insecticide permethrin has a tolerance of 1.0 ppm on peaches, but is not allowed (tolerance = 0 ppm) on plums. Due to the similarity of the pesticides found on both crops, it seems likely that the same pesticide mixture was applied to both crops. The DCP notified the grower of the violation, no enforcement action was taken by the DCP.

A sample of spinach grown in the US outside Connecticut was found to contain residues of the insecticide cypermethrin (0.218 ppm). Cypermethrin is a pyrethroid ester insecticide with a chemical structure very similar to permethrin, but containing an additional nitrile (-C=N)

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[1] Further impacts of the 2006 findings are presented in Krol et al, 2007.

[2] 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.

functional group. Permethrin is used fairly commonly on spinach for control of leaf miners and other insects and has a tolerance of 20 ppm. Cypermethrin, conversely, which is registered for use on numerous other commodities, is not registered for use on spinach. The DCP notified the FDA of this finding. No recall was initiated by the FDA.

In 2007, a total of 24 samples of organically labeled produce[3] samples were tested for pesticide residues. Of these samples, four were fresh, the remainder were processed foods. Eight samples were from the US, ten were foreign (4 from China, 2 from Mexico and one each from Canada, Peru, Serbia and Turkey), and six were of unknown origin. There was only a single organically labeled sample grown in Connecticut included in the survey. Four pesticide residues were found on three of the 24 samples resulting in 12.5% of the organically labeled produce containing pesticide residues. Specifically, a frozen sample of spinach of unknown origin was found to contain DDE (0.01 ppm) and endosulfan (0.034 ppm); a frozen sample of blackberries from Serbia was found to contain 0.007 ppm fenhexamid; a sample of apple cider from Pennsylvania was found to contain 0.001 ppm boscalid.

Findings of carbendazim were reported in a total of eight (8) samples in 2007, specifically in one (1) sample of fresh pears, three (3) samples of fresh apples, and four (4) samples of apple cider. All of these samples were either grown in, and/or processed in, Connecticut. Carbendazim was found in these samples between 0.020 and 0.073 ppm with an average value of 0.041 ppm. Carbendazim (itself) has no tolerance on any food commodity in the US, although it is still used in other parts of the world as a fungicide. It may appear that these eight samples should be violative. Carbendazim, however, is also known to be a metabolite (breakdown product) of two other fungicides commonly used in the production of pears and apples, namely benomyl and thiophanate methyl. Anastassiades and Schwack have studied and reported their findings of the breakdown and degradation of benomyl and thiophanate methyl to carbendazim in samples of fruits and vegetables. The work also evaluated the degradation of these parents during the extraction of samples of produce and was published in a peer reviewed paper (Anastassiades, 1998).

From a regulatory standpoint, when carbendazim residues are found they are reported as the parent from which the residue is derived. Thus, for example, if a sample of apples is found to contain 0.005 ppm thiophanate methyl and 0.006 ppm carbendazim, a value of 0.011 ppm thiophanate methyl and metabolites would be reported. Benomyl (40CFR180.294) has a tolerance on both apples and pears of 7.0 ppm, while thiophanate methyl (40CFR180.371) has a tolerance of 2.0 ppm on apples and 3.0 ppm on pears. If carbendazim is found in the absence of either parent, we have interpreted the guidance published in the Federal Register such that provided either of the parents of carbendazim (benomyl or thiophanate methyl) have a tolerance on the given crop on which it is found, and the level of carbendazim found is not in excess of the highest tolerance of either parent, then the presence of carbendazim in the absence of either of the parents is not a violation of Federal law. Thus, for the sake of reporting the eight findings this year, we have chosen to report in the following manner, for example on pears: 0.020 ppm of carbendazim was detected likely due to the application of benomyl 40CFR180.294 T=7.0 ppm or thiophanate methyl 40 CFR180.371 T=3.0 ppm.

CONCLUSIONS

In 2006, we demonstrated the usefulness of employing the QuEChERS methodology in our market basket pesticide monitoring program (Krol, 2007). By replacing our traditional VegPrep method with the QuEChERS method in our market basket survey in 2007 solvent use was reduced by 26.4 Liters for the 198 samples analyzed. This translates to 26.4 L of solvent that was not purchased, and perhaps more importantly did not require costly disposal as hazardous waste. In the current work, we have demonstrated the usefulness of user-generated MS libraries of AI's as an aid in the determination of pesticide residues in extracts from our market basket work. This combined work has resulted in an increase in the number of pesticide residues detected and a decrease in the average value of pesticides found since 2005.

Of the 198 samples tested for pesticide residues in 2007, 120 (60.6%) samples contained 327 pesticide residues of which six (6) were found to be illegal. This compares to 122 (67.4%) samples containing pesticide residues in 2006 and 70 (42.9%) in 2005 (Table 3). The results of all these analysis have been forwarded to the DCP for regulatory enforcement purposes. In the case of out of state violative samples, the DCP forwarded the laboratory's analytical results to the FDA. In the case of peas from Guatemala, this work led to the automatic detention of future shipments.

Our advances in extracting and analyzing pesticide residues have dramatically changed the outcomes of the market basket survey results over the past two years. Opposed to the majority of the samples analyzed (~60%) being free from pesticide residues, our advancements point to the fact that the majority of the samples in our market basket survey, a little over 60%, contain pesticide residues. Produce labeled as 'Organic' is not free from pesticide residues. In 2007, 12.5% of the organic produce tested contained pesticides,

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[3] Produce bearing the 'Organic' label must comply 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.

compared to 25% in 2006, and 20% in 2005.

The reader should note that although the majority of the samples tested contain pesticide residues, the levels at which these pesticides are detected is very low in comparison to their tolerances. The average pesticide residue in 2007 was 0.163 ppm, and the average tolerance for those residues was 6.8 ppm (excluding the six no tolerance violations). The average residue was 41.7 % lower than the average tolerance. The work contained herein continues to ensure that the food sold in Connecticut contains pesticide residues that are within the guidelines of US Federal Law.

ACKNOWLEDGEMENTS

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Table 1: Commodities Studied and Frequency of Pesticides Found

	Total Samples (Samples w/ Pesticides)	Total Pesticides	Acetamiprid	Azinophos-Me	Azoxystrobin	BHC	Bifenthrin	Boscalid	Captan	Carbaryl	Carbendazim*	Chlorothalonil	Chlorpyrifos	Clothanadin	Coumaphos	Cyhalothrin	Cypermethrin	Cyprodinil	Dacthal (DCPA)	DDT	Dicofol	Dimethomorph	Diphenylamine	Endosulfan	Fenbuconazole	Fenhexamid	Fenpropathrin	Fenpyroximate	Fenvalerate	Fludioxonil	Fluvalinate	Imazalil	Imidacloprid	Kresoxim-Me	Malathion	Metalaxyl	Methomyl	OPP	Oxamyl	Pendimethalin	Permethrin	Phosmet	Thiabendazole	Thiacloprid	Thiamethoxam	Thiophenate-Me	Trifloxystrobin
Apples	37 (36)	140	7	2				11	24	4	3		1			2					1		7	1			7	2					9	1			1		1	6		30	1	2	2	8	7
Beans	8 (2)	2					2																																								
Blackberries	2 (1)	1																								1																					
Blueberries	4 (3)	10			1			2	1									1							1		1										1					2					
Brocolli Rabe	1 (1)	1																																		1											
Cabbage	1 (1)	1																															1														
Cantaloupe	1 (1)	2										1																									1										
Cider	15 (14)	47	9	4				4		4	4												3										2						1			8	4	2		1	1
Corn	10 (1)	1																																			1										
Cucumbers	4 (2)	3																				1		2																							
Currant	2 (1)	1								**1**																																					
Ginger, Root	5 (1)	1				1																																									
Honey	5 (5)	10													5																5																
Kiwi	2 (1)	1																								1																					
Lemons	1 (1)	1																														1															
Lettuce	4 (2)	3								1								1	1																												
Nectarines	1 (1)	3						1																	1				1																		
Onions. Green	1 (1)	1										1																																			
Parsnips	1 (1)	1								1																																					
Peaches	8 (5)	14						2	3	1														2	2				1												1	2					
Pears	8 (7)	33	1	1			1	3	1		1			2		1							1	1			2						1	1			1			1		5		1	2	3	3
Peas	20 (7)	8								1		**2**	1											1											2						**1**						
Peppers	6 (1)	1																																			1										
Pineapples	1 (1)	1							1																																						
Plums	1 (1)	4						1	1															1																	**1**						
Pomegranate	1 (1)	2																												1			1														
Soybeans	3 (1)	1																		1																											
Spinach	4 (3)	4															**1**			1				1																	1						
Squash	9 (8)	12						1				2								2				7																							
Strawberries	8 (6)	14							1	1								3								4	2								1		2										
Tomatoes	9 (3)	3										1										1																1									
	183 (120)	327																																													
	15 (0)	Samples not included above:Cherries (2), Cranberries (1), Collard Greens (1), Guava (1), Mangoes (3), Oranges (1), Rice (4), & Wheat (2) which contained no pesticide residues.																																													
	198 (120)	327	17	7	1	1	3	25	32	14	8	7	2	2	5	3	1	5	1	4	1	2	11	16	4	6	12	2	2	1	5	1	14	2	3	1	8	1	2	7	4	47	5	5	4	12	11

*Carbendazim was reported in those cases in which no parent benomyl or thiophanate methyl was found.

Violative samples are denoted in **Bold Red** print.

All pesticides are reported as Active Ingredient (AI) plus their respective metabolites.

Table2: Pesticide Residues Found by Instrument by Quarter 2007

Pesticide	1st Quarter			2nd Quarter			3rd Quarter			4th Quarter			Yearly Total
	1st Q Totals	Detected By GC	LC	2nd Q Totals	Detected By GC	LC	3rd Q Totals	Detected By GC	LC	4th Q Totals	Detected By GC	LC	
Acetamiprid							3		3	14		14	17
Azinophos-Methyl										7		7	7
Azoxystrobin							1	1	1				1
(BHC)							1	1					1
Bifenthrin	2	2								1		1	3
Boscalid							13	8	12	12	1	12	25
Captan				1	1		11	11		19	19		31
Carbaryl	6	1	5	1		1				8 **(1)**		8 (1)	15
Carbendazim*										8		8	8
Chlorothalonil	4 **(2)**	2 (1)	4 (2)				3	3					7
Chlorpyrifos	1		1							1		1	2
Clothanadin										2		2	2
Coumaphos										5		5	5
Cyhalothrin										3	3		3
Cypermethrin	1 **(1)**	1 (1)											1
Cyprodinil				4	3	4	1	1	1				5
DCPA				1	1								1
DDT and Metabolites	2	2					2	2					4
Dicofol										1	1		1
Dimethomorph	2		2										2
Diphenylamine										11	7	10	11
Endosulfan	3	3		1	1		10	10		2	2		16
Fenbuconazole							4	4	4				4
Fenhexamid	3	3	2	3	2	1							6
Fenpropathrin				2	2	1	3	3	3	7	4	7	12
Fenpyroximate										2		2	2
Fenvalerate							2	2					2
Fludioxonil										1		1	1
Fluvalinate										5		5	5
Imazalil	1	1	1										1
Imidacloprid & Metabolites							3		3	11		11	14
Kresoxim Methyl										2	2		2
Malathion	3	2	1										3
Metalaxyl										1		1	1
Methomyl	4		4	1		1	1		1	2		2	8
OPP							1	1					1
Oxamyl										2		2	2
Pendimethalin							6		6	1		1	7
Permethrin	2 **(1)**	2 (1)					2 **(1)**	2 (1)					4
Phosmet							14	2	14	33	22	33	47
Thiabendazole	1	1								4	4	4	5
Thiacloprid & Metabolites										5		5	5
Thiamethoxam							3		3	1		1	4
Thiophenate-Methyl							2		2	10		10	12
Trifloxystrobin							2	2	2	9	1	9	11
Sum Totals	35			14			88			190			327

Reported Violations are shown in **Parenthetical Red Boldface.**

The instrument by which they were detected is denoted parenthetically.

*Carbendazim was reported in those cases in which no parent benomyl or thiophanate methyl was found.

Table 3: Summary of All Market Basket Samples, Including Organic and Processed Food 1990 - 2007.

Year	Total Samples Tested	Samples with NO Residues	Average Pesticide Residue (ppm)	Samples with Residues Within EPA Tolerances	Samples with Residues Over EPA Tolerances	Samples with Residues with NO EPA Tolerance
1990	418	186 (44.5)	0.147	230	0	2
1991	285	190 (66.7)	0.161	94	0	1
1992(d)	273	179 (65.6)	0.291	89	1	4
1993	443	305 (68.8)	0.435	128	3	7
1994	545	414 (76.0)	0.342	125	1	5
1995	444	307 (69.1)	0.513	129	0	8
1996	327	188 (57.5)	0.321	134	1(a)	4
1997	412	266 (64.6)	0.248	144	0	2
1998	180	115 (63.9)	0.528	63	0	2
1999(e)	195	115 (59.0)	0.664	72	0	8
2000	145	90 (62.1)	0.613	54	1	0
2001	315	201 (63.8)	1.291	112	0	2
2002	206	137 (66.5)	0.732	68(b)	0	1
2003	298	195 (65.4)	0.856	95	1	7(c)
2004	197	122 (61.9)	0.596	71	1	3
2005	163	93 (57.1)	0.959	67	0	3
2006(f)	181	59 (32.6)	0.221	102	0	20
2007	198	78 (39.4)	0.163	114	0	6
Total	**5225**	**3240**	**0.505**	**1891**	**9**	**85**

(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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