PESTICIDE RESIDUES IN PRODUCE SOLD IN CONNECTICUT IN 2009

WALTER J. KROL, BRIAN D. EITZER, TERRI ARSENAULT AND
JASON C. WHITE

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Walter J. Krol, Brian D. Eitzer, Terri Arsenault and Jason C. White
Department of Analytical Chemistry
The Connecticut Agricultural Experiment Station

Introduction

The Department of Analytical Chemistry at the Connecticut Agricultural Experiment Station (CAES), in collaboration with the Connecticut Department of Consumer Protection (DCP), conducts an annual market basket survey of produce sold in Connecticut for pesticide residues. The results of the pesticide monitoring studies have been published, at least in part, on an annual basis since 1963 (Krol *et al.*, 2006). The goals of this program are: 1) to ensure that pesticides are used in accordance with their label and 2) to ensure that the public is protected from the deliberate or accidental misuse of pesticides. The 2009 data help to clarify and define the use of pesticides in the production of the food we consume. The findings of the 179 samples analyzed in the calendar year 2009 are summarized herein.

To be able to enforce the Environmental Protection Agency, (EPA) mandated tolerances, both the Food and Drug Administration (FDA) and DCP must know the quantity and the type of pesticide residues present in foodstuffs offered for sale[1]. In Connecticut, the DCP relies on the laboratories of the Department of Analytical Chemistry at the CAES to perform analysis of foods sold within the state for pesticide residues. The Connecticut 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. In the current year, samples were obtained from 96 Connecticut farms, producers, retailers, and wholesale outlets. The program determines if the amounts and types of pesticides found on fruits and vegetables adhere to the tolerances set by the EPA. These tolerances are continually updated and available in the electronic Code of Federal Regulations (e-CFR, 2010). 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

[1] For a more complete overview of the Federal Agencies involved, their roles, and a discussion on tolerances see Krol *et al* 2006 and the references cited therein.

allowed (no tolerance). In all cases, the results of the laboratory 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 may perform 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. For violations occurring in samples produced outside of Connecticut, the DCP notifies the local field office of the FDA in Hartford of the findings.

Methods

Sample Collection:

Samples of produce grown in Connecticut, other states, and foreign countries were collected at 96 different Connecticut farms, producers, retailers, and wholesale outlets by inspectors from the DCP. The samples collected were brought to our laboratory in New Haven by inspectors for pesticide residue testing. In all cases, these market basket samples were collected without prior knowledge of any pesticide application.

Sample Homogenization:

In all cases, samples were processed according to the Pesticide Analytical Manual (PAM, 1994). The vast majority of the samples were prepared in their natural state as received, unwashed and unpeeled. 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; AOAC, 2007; Method 2007.01) 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 part per million (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) all available from Mallinckrodt Baker, Inc., were added. 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), together with 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 reconstituted 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.

Instrumental Analysis:

Samples extracted by the QuEChERS method were concomitantly 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) port 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 Enhanced MSD Chemstation Software version E.02.00.493. Deconvolution and identification of pesticides in the mass spectra of samples were aided by the use of the *A*utomated *M*ass spectral *D*econvolution and *I*dentification *S*ystem (AMDIS) with a user constructed library. 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 (H_2O/0.1*N* HCOOH) to B (100% MeOH/0.1*N* HCOOH) over 20 min; hold 100% B for 10 min. The column eluant was interfaced to a Thermo-Electron LTQ ion trap mass spectrometer. The mass spectrometer was operated in the positive ion electrospray mode with most pesticides being determined using MS/MS selective reaction monitoring. Data were collected and analyzed using Xcalibur® software version 2.0.

Reproducibility of Results:

All samples examined in this work were individually homogenized, extracted and analyzed by GC and LC once. Statistical analysis obtained through inter and intra-laboratory studies over a wide range of pesticides, pesticide concentrations, and matrices have demonstrated that this is sufficient to obtain accurate quantitation of pesticide residue concentrations from the extract of a single sample (AOAC, 2007; Method 2007.01). Further proof of this was obtained in unpublished work conducted in our laboratories on violative samples. All violative samples were re-extracted, analyzed, and quantitated in duplicate using portions of the original sample retained from homogenization step. One of the duplicate samples was spiked with the pesticide in question at a concentration slightly above the originally determined value. Quantitative values of these extracts were compared to the concentration found in the original analysis.

Results and Discussion

During the 2009 calendar year, a total of 179 samples, representing a variety of fresh and processed foods, were tested. Of those 179 samples, 132 (73.7%) were fresh produce, 47 (26.3%) were processed products. The findings of this survey are summarized in Table 1, for fresh, and Table 2 for processed foods. Pesticide residues were found in 104 samples of fresh produce (78.8%) and 35 (74.5%) samples of processed products. The majority of the total samples analyzed, 139 (77.7%), were found to contain residues of at least one pesticide, while the remaining samples, 40 (22.3%), were found to be free of any detectable residues. A total of 458 pesticide residues comprised of 61 different Active Ingredients (AI's) were found during the course of this work. The number of residues and different AI's found in 2009 surpass those found in any previous year of this study. Of those samples containing residues, 126 (70.4% of the total samples) contained permissible pesticide levels (non-violative residues); thirteen samples (7.3% of the total samples) contained 20 residues which were not allowed (violative samples). Of the violative samples, eleven (8.3% of the total fresh samples) were found on fresh and two (4.3% of the total processed samples) on processed produce.

A total of eight residues of seven different AI's were found on five (29.4%) of the seventeen organically grown food samples tested as part of this survey. This is the highest percentage of pesticide residues found on organic produce in the history of the residue testing program at CAES. On average, 19.6% of organic food tested from 2006-2008 using the QuEChERS method and 13.4% of the produce tested from 2000-2008 were found to contain pesticide residues. It should be noted that from 2000-2008 only 36 residues were found on a total of 175 organic samples with 21 of these being found from 2006-2008 (68 samples). The increasing numbers of organic samples found to contain residues is likely due to the lower pesticide levels being found in our program (*Vida infra).* None of the residues found on organic produce in 2009 were tolerance violations nor were they in violation of the National Organic Program (NOP) exclusion from sale provision related to pesticide residue testing. In general terms, pesticide residues are allowed on organic produce provided that the residues are at levels below five percent of the EPA tolerance for the specific residue on the specific crop[2] (NOP, 2004). The reader is also referred to Krol *et al.*, 2006 for a more comprehensive discussion of the NOP.

It should be noted that the CAES solely performs the analytical analysis of samples on behalf of the CT DCP, wherein regulatory authority lies. Enforcement actions (or lack thereof) taken by the DCP or the FDA are not always communicated back to the performing laboratories at the CAES. In those cases where the laboratory is made aware of the outcome (i.e. recalls, etc.), details of such are provided in the text below.

The thirteen violative samples found were comprised of eleven different commodities as can be seen in Tables 1 & 2. There was one sample analyzed that resulted in an over tolerance violation, two samples that contained separate residues that were each individually over tolerance and no tolerance, and there were ten samples which contained fifteen residues for which there is no tolerance. Twelve of the samples were from the United States (US), nine from Connecticut and the foreign sample was from Canada. Violations were found on processed samples of apple cider (1 ME) and celery (1 Canada), and on fresh samples of three apples (2 CT; 1 NY), one sample each of chard, chives, lettuce, peach, pear, plum and strawberry all grown in Connecticut, as well as one sample of sweet potato grown in the US outside Connecticut.

[2] NOP Title 7 Part 205 § 205.671 Exclusion from organic sale states: 'When residue testing detects prohibited substances at levels that are greater than 5 percent of the Environmental Protection Agency's tolerance for the specific residue detected or unavoidable residual contamination, the agricultural product must not be sold, labeled, or represented as organically produced. The Administrator, the applicable State organic program's governing State official, or the certifying agent may conduct an investigation of the certified operation to determine the cause of the prohibited substance.'

There were three samples of fresh apples (2 CT; 1 NY), which contained illegal residues of the insecticide chlorpyrifos (0.017-0.089 ppm), all of which were over the tolerance of 0.010 ppm resulting in the three over tolerance violations. The two samples from the same Connecticut grower were also found to contain the fungicide iprodione (0.020-0.080 ppm) which is not allowed on apples, resulting in concurrent no tolerance violations of these samples. The results of these analyses were forwarded to the DCP, and as appropriate to the FDA, and the outcome of the actions taken by these agencies is unknown at the time of this writing.

The violative processed samples were comprised of a sample of apple cider from Maine which was found to contain 0.061 ppm of the fungicide fenhexamid (no tolerance) and a sample of celery from Canada which was found to contain residues of chlorpyrifos (0.002 ppm) and the herbicide pendimethalin (0.001 ppm) (both no tolerance). The results of these analyses were forwarded to the DCP who in turn forwarded them to the FDA. A review of the FDA Recalls, Market Withdrawals & Safety Alerts website confirmed that no recalls were issued for these products by the FDA (FDA Recalls; 2010).

It should also be noted that the cider sample from Maine was also found to contain 0.125% potassium sorbate and 0.004% sodium benzoate. CAES routinely performs analysis for potassium sorbate and sodium benzoate on samples of juices and ciders to help enforce labeling laws; these results are included in Table 2. These chemicals are routinely used in foods to preserve freshness by inhibiting mold growth and preventing spoilage and are Generally Recognized as Safe (GRAS) by the FDA (GRAS, 2010). Because they are introduced into food, they must also be declared on the label of the container as an additive. In the case of this sample, no such declaration was made. The maximum amount of sodium benzoate that can be added to food is 0.1% (Pylypiw *et al.; 2000;* e-CFR Sodium Benzoate, 2006) whereas potassium sorbate is typically used at 0.1 – 0.2% (Pylypiw *et al., 2000*; e-CFR Potassium Sorbate, 2010). The retailer was informed of the violative laboratory results by the DCP and additionally of the fact that the product was produced by an unlicensed manufacturer making it unlawful for sale in Connecticut. The CT DCP forwarded the results of these analyses to the State of Maine and FDA. As of this writing, the outcome of this investigation was unknown by DCP.

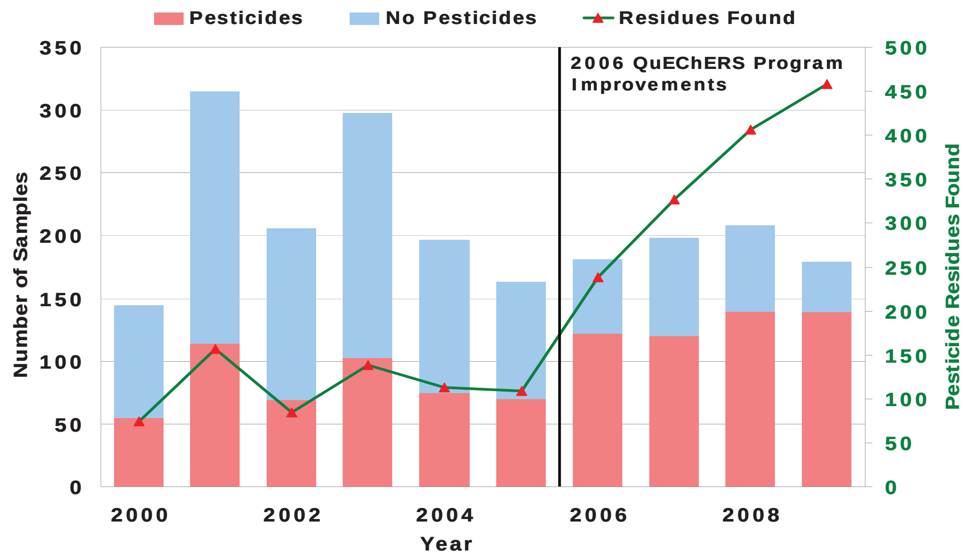
The sample of sweet potato grown in the United States but of unknown specific origin was found to contain five different pesticide residues. Three of these pesticides were not allowed on sweet potato, resulting in the no tolerance violation. The illegal residues found were the fungicide imazalil (0.001 ppm) and the insecticides permethrin (0.014 ppm) and dimethoate (0.002 ppm). The results of the analysis were forwarded to the FDA by the CT DCP, and the results of the investigation are unknown.

The remaining seven samples which contained nine residues were all grown in Connecticut and resulted in seven no tolerance violations. A sample of chard contained chlorpyrifos (0.003 ppm); a chive sample contained illegal residues of three pesticides; the insecticide fipronil (0.002 ppm); the herbicide metolachlor (0.008 ppm); and the fungicide thiabendazole (0.001 ppm). A lettuce sample contained residues of the herbicide oxyfluorfen (0.002 ppm). Samples of peaches and plums, both from the same grower, were found to contain the insecticide thiacloprid (0.013 and 0.009 ppm respectively). There was a pear sample which was found to contain residues of the fungicide fenbuconazole (0.003 ppm), and a sample of strawberries that was found to contain residues of the insecticide phosmet (0.003 ppm). Letters were sent to the Connecticut growers by the DCP notifying them of the violations.

Program Improvements

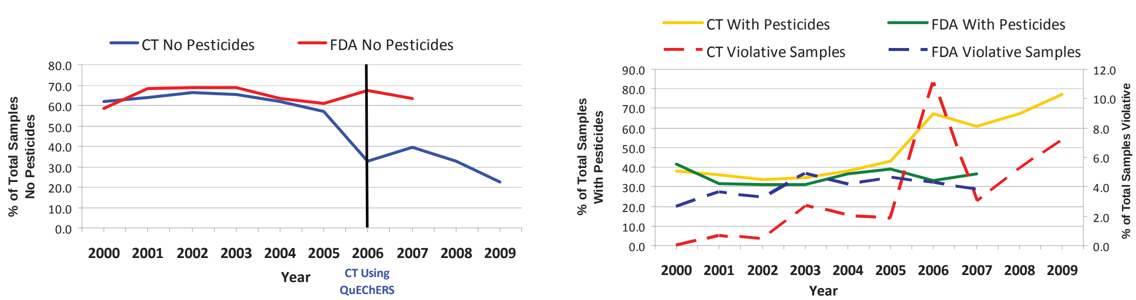
Summary results of the CAES pesticide residue program from 2000 to present are presented in Figure 1. The discord observed between the QuEChERS timeframe of 2006-2009 with that of the pre-QuEChERS interval (2000-2005) is the result of several major (and ongoing) improvements made in our program as described in previous work (Krol *et al.*; 2007, 2009, 2010). During the pre-QuEChERS timeframe, 63.3% of the samples tested contained no detectable pesticides residues and there were, on average, 1.3 residues found on those samples containing pesticides. These results correlated well with those of the FDA pesticide residue monitoring program since 1990 and are compared in Figure 2 below and more comprehensively in previous work (Krol *et al.*, 2010). Since 2006, when the improvements to our program were initiated, on average, 31.0% of the samples tested were found to contain no detectable pesticide residues and the average number of residues found on samples which contained residues

Figure 1: Pesticide Residues in Food Sold in Connecticut 2000-2009.



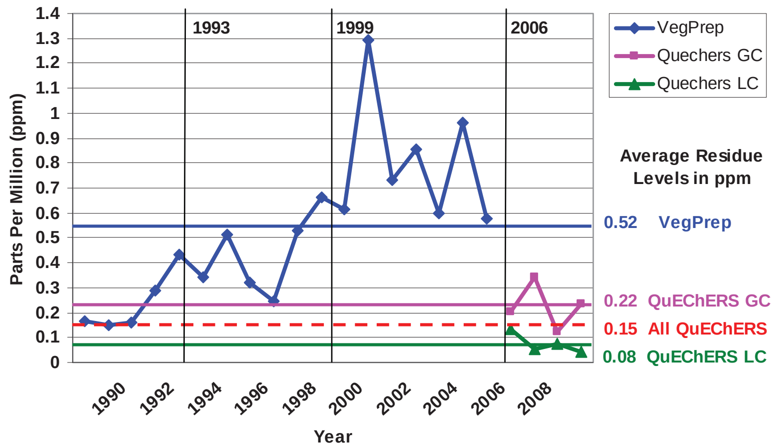
increased to 2.7. Comparatively, in the 2006-2008 timeframe, we reported that 33.8 % of the samples examined contained no residues and the average number of residues per sample containing residues was 2.5 (Krol *et al.*, 2010). The variation observed by including the 2009 data into the 2006-2008 average is ultimately attributable to efforts focused on screening for greater numbers of AI's through the construction of MS libraries.

Figure 2: Comparison of CT and FDA Results 2000 – 2009.



It is interesting to highlight our recent advances by comparing the average concentration of all the pesticide residues found on the samples tested in a given year. In 2009, the average residue value was 0.09 ppm, and in the 2006–2009 timeframe employing QuEChERS, it was 0.15 ppm. As can be seen in Figure 3, the average yearly residue values during the QuEChERS timeframe is nearly identical to the 0.16 ppm average found in the 1989–1991 timeframe when our modern residue program was begun. The QuEChERS extraction protocol provides a ten-fold concentration factor over our older VegPrep method overcoming the reduced sensitivity provided by the use of MS detection (Figure 3). This effectively cancels the drop in sensitivity introduced by employing MS detection such that the average residue value in ppm employing MS is similar to that obtained using the more specific highly sensitive detectors.

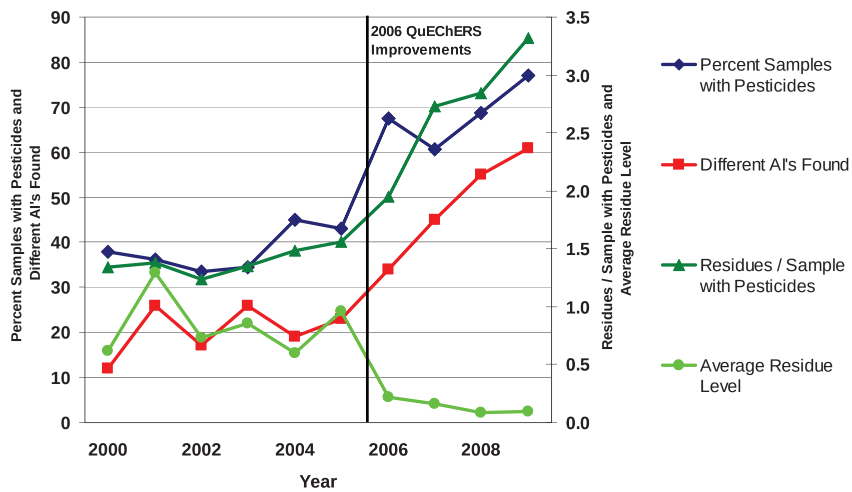
Figure 3: Comparison of Pesticide Residue Levels 1989 - 2009.



During the years 1989-1993, highly selective, specialized and sensitive detectors were employed which were only able to detect on average seventeen different AI's based solely upon their GC retention time. In 1993, with the introduction of MS, the average number of residues that were found began to rise. We moved away from using these selective detectors, choosing to focus more on the use of MS. The use of MS provided less sensitivity but allowed for the identification a greater range of pesticides containing varying chemical makeup. The use of MS additionally provides unequivocal identification of the pesticide by obtaining the unique chemical 'fingerprint' of the chemical analyte. In 2009, thirty-seven different AI's were identified and confirmed by GC/MS and a total of sixty-one different AI's were identified through the combination of GC/MS and LC/MS matching to libraries created at CAES. This is the greatest number of AI's found in any year of this survey. From 1989–2005 (pre-QuEChERS), on average a total of 17.9 different AI's were found each year.

Figure 4 graphically depicts the improvements to our program. Expanded screening clearly led to larger numbers of different AI's being found. The concentration factor gained by employing QuEChERS combined with the more sensitive instrumentation used in the detection of pesticide residues allows lower levels to be determined by MS. The detection of residues at lower levels has led to an increase in the number of residues per sample and the overall number of samples containing pesticide residues. The use of our current methodology allows us to obtain a clearer picture of the numbers of pesticides that are actually consumed in the food we eat (Figure 1) and gives us a better understanding of the prevalence of pesticides in our diet.

Figure 4: Graphical Depiction of Program Improvements.



Conclusions:

In the current work, a greater number of AI's (61) and pesticide residues (458) were detected than any other year in our survey. The vast majority of the residues (95.6%) were found to be within the tolerances set by the EPA. Of the 178 samples analyzed, 139 (77.7%) were found to contain pesticide residues. Residues were found in 78.8% of the fresh, 74.5% of the processed and 29.4% of the organic samples analyzed.

Nearly all the food we eat, with the exception of organically grown produce, has been treated with pesticides during the course of its production. If the pesticides used during the production of this food have been used in accordance with the approved use of the pesticidal product, the levels resulting on the food will be below the EPA tolerance. In the past, owing to the sensitivity and specificity of the instruments used at the CAES for detection, many of the residues have gone undetected. Owing to the increased sensitivity of our instrumentation and the QuEChERS methodology for the extraction of the residues from samples, we are detecting greater numbers of pesticides at lower levels. The results of this work allow the consumer to gain a better understanding of the prevalence and levels of pesticide residues in the food they consume.

Acknowledgements:

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References:

Anastassiades, M., Lehotay, S.J., Stajnbaher, D. and Schenck, F.J., (**2003**) "Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce" J AOAC Int., 86:412-431. See also: http://www.QuEChERS.com/

AOAC (**2007**) Official Methods of Analysis; Method 2007.01, "Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate." First Action, 2007.

e-CFR [Electronic Code of Federal Regulations]. (**2010**) Title 40, Parts 180, 185, and 186. http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?&c=ecfr&tpl=/ecfrbrowse/Title40/40tab_02.tpl

e-CFR Potassium Sorbate [Electronic Code of Federal Regulations]. (**2010**) Title 27 §24.246 CFR 182.3089. http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=854ae8dad832d0691586c6cf6ed8b20b&rgn=div8&view=text&node=27:1.0.1.1.19.12.295.7&idno=27

e-CFR Sodium Benzoate [Electronic Code of Federal Regulations]. (**2006**) Title 21 CFR 184.1733. http://edocket.access.gpo.gov/cfr_2006/aprqtr/pdf/21cfr184.1733.pdf

FDA Recalls, Market Withdrawals and Safety Alerts (**2010**) available at: http://www.fda.gov/safety/recalls/default.htm

GRAS [Generally Recognized as Safe]. (**2010**) Federal Register Volume 75 Title 21, Part 182 Chemicals Generally Recognized as Safe. http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&rgn=div5&view=text&node=21:3.0.1.1.13&idno=21#PartTop

NOP [National Organic Program]. (**2004**) Federal Register Volume 69 Title 7, Part 205 § 205.671 *Exclusion from Organic sale*.

PAM [Pesticide Analytical Manual]. (**1994**). Volume I, 3rd Edition, Updated October, 1999, C.M. Makovi, ed., U. S. Food and Drug Administration,

Office of Plant and Dairy Foods and Beverages. Available at:
http://www.cfsan.fda.gov/~frf/pami1.html

Pylypiw H., Grether, M.T., (**2000**) “Rapid high-performance liquid chromatography method for the analysis of sodium benzoate and potassium sorbate in foods” J Chrom. A, 883:229-304.

Krol, W.J., Arsenault, T., Mattina, M. J. I., (**2006**) ‘Pesticide Residues in Produce Sold in Connecticut 2005.’ Bulletin 1006. The Connecticut Agricultural Experiment Station, New Haven, CT. Available at:
http://www.caes.state.ct.us/Bulletins/bulllist.htm

Krol, W.J., Eitzer, B.D., Arsenault, T., Mattina, M. J. I., (**2007**) ‘Pesticide Residues in Produce Sold in Connecticut 2006 with a Comparison of Two Sample Preparation Methods.’ Bulletin 1012. The Connecticut Agricultural Experiment Station, New Haven, CT. Available at:
http://www.caes.state.ct.us/Bulletins/bulllist.htm

Krol, W.J., Eitzer, B.D., Mattina, M. J. I., Arsenault, T., (**2009**) ‘Pesticide Residues in Produce Sold in Connecticut 2007.’ Bulletin 1024. The Connecticut Agricultural Experiment Station, New Haven, CT. Available at:
http://www.caes.state.ct.us/Bulletins/bulllist.htm

Krol, W.J., Eitzer, B.D., Mattina, M. J. I., Arsenault, T., (**2010**) ‘Pesticide Residues in Produce Sold in Connecticut 2008. Technical Bulletin TB3. The Connecticut Agricultural Experiment Station, New Haven, CT. Available at:
http://www.ct.gov/caes/cwp/view.asp?a=2826&q=455190

Table 1: Summary of Pesticides Found in Fresh Fruits and Vegetables Sold in Connecticut in 2009.

Commodity / Origin / Pesticide	Samples with Residues (Total)	Found by LC, GC or Both	Number of Times Detected	Residue Range (ppm)	Average Residue (ppm)	EPA Tolerance (ppm)
Apples (25 Samples; 2 Foreign; 1 *Organic*; **3 Violations**)						
Connecticut	21 (21)					
Acetamiprid		LC	2	0.003-0.040	0.022	1
Azinphos Methyl		LC	1	0.001		1.5
Boscalid		Both	7	0.001-0.096	0.034	3
Captan		GC	8	0.028-1.322	0.364	25
Carbaryl		Both	2	0.150-0.235	0.192	12
Carbendazim (Metabolite)		LC	5	0.020-0.047	0.036	none*
Chlorpyrifos		**Both**	**2**	**0.017-0.089**	**Over Tolerance**	**0.01**
Cyhalothrin, *lambda*		GC	1	0.019		0.3
Cyprodinil		LC	1	0.003		0.1
Difenoconazole		LC	2	0.001-0.002	0.002	1
Fenbuconazole		LC	4	0.001-0.008	0.006	0.4
Fenpropathrin		LC	2	0.007-0.010	0.009	5
Fenpyroximate		LC	1	0.012		0.4
Fenvalerate		Both	2	0.005-0.012	0.008	2
Imidacloprid		LC	6	0.001-0.075	0.026	0.5
Indoxacarb		LC	2	0.006-0.012	0.009	1
Iprodione		**LC**	**2**	**0.007-0.008**	**No Tolerance**	**0**
Pendimethalin		LC	1	0.002		0.1
Phosmet		Both	15	0.006-0.614	0.133	10
Thiacloprid		LC	4	0.002-0.037	0.011	0.3
Thiophanate Methyl		LC	10	0.033-0.742	0.242	2
Trifloxystrobin		Both	6	0.001-0.024	0.007	0.5
New York	2 (2)					
Azinphos Methyl		LC	2	0.001-0.007	0.004	1.5
Boscalid		Both	2	0.027-0.168	0.094	3
Captan		GC	2	0.342-0.512	0.427	25
Chlorpyrifos		**Both**	**1**	**0.028**	**Over Tolerance**	**0.01**
Phosmet		Both	2	0.006-0.138	0.060	10
Thiacloprid		LC	2	0.001-0.166	0.084	0.3
Thiophanate Methyl		LC	2	0.037-0.166	0.102	2
Trifloxystrobin		LC	1	0.003		0.5
Foreign (N. Zealand)	1 (1)					
Thiacloprid		LC	1	0.011		0.3
Organic						
Chile	0 (1)					
Apricots (1 Sample; 1 Unknown)						
Unknown	1 (1)					
Boscalid		LC	1	0.003		1.7

Beans, Snap (8 Samples; 1 Unknown)						
Connecticut	4 (5)					
Acephate		LC	1	0.006		3
Azoxystrobin		Both	1	0.026		3
Boscalid		LC	1	0.009		1.6
Chlorothalonil		LC	3	0.004-0.06	0.074	0.1
DDE		GC	1	0.002		0.2
Endosulfan		GC	1	0.002		2
Florida	1 (1)					
Azoxystrobin		LC	1	0.003		3
Thiophanate Methyl		LC	1	0.190		0.2
Virginia	1 (1)					
Acephate		LC	1	0.261		3
Carbendazim (Metabolite)		LC	1	0.001		none*
Unknown	1 (1)					
Chlorothalonil		LC	1	0.013		0.1
Cyhalothrin, *lambda*		GC	1	0.027		0.2
Metalaxyl		Both	1	0.004		0.2
Thiophanate Methyl		LC	1	0.049		0.2
Blueberries (9 Samples; 1 *Organic*)						
California	1 (1)					
Boscalid		Both	1	0.014		1.7
Fenbuconazole		Both	1	0.002		0.3
Malathion		Both	1	0.024		8
Connecticut	4 (5)					
Captan		GC	1	0.122		20
Carbendazim (Metabolite)		LC	2	0.001-0.015	0.008	none*
Fenbuconazole		LC	1	0.013		0.3
Iprodione		LC	1	0.001		15
Phosmet		LC	3	0.005-0.077	0.038	10
Florida	1 (1)					
Cyprodinil		Both	1	0.007		3
New Jersey	1 (1)					
Boscalid		Both	1	0.059		1.7
Captan		GC	1	0.029		20
Organic	0 (1)					
Connecticut						
Bok Choy (1 Sample)						
Connecticut	0 (1)					
Cantaloupe (2 Samples; 2 Foreign)						
Foreign (Guatemala)	1 (1)					
Azoxystrobin		GC	1	0.015		0.3
Boscalid		Both	1	0.013		1.6
Chlorothalonil		LC	1	0.020		5
Methomyl		LC	1	0.021		0.2
Pyriproxyfen		Both	1	0.005		0.1
Thiabendazole		Both	1	0.002		15

(Costa Rica)	1 (1)					
Carbendazim (Metabolite)		LC	1	0.002		none*
Metalaxyl		LC	1	0.071		1
Methomyl		LC	1	0.003		0.2
Carrots (1 Sample)						
Connecticut	0 (1)					
Chard, Swiss (1 Samples; **1 Violation**)						
Connecticut	1 (1)					
Chlorpyrifos		**LC**	**1**	**0.003**	**No Tolerance**	**0**
Cypermethrin		GC	1	0.050		10
Methomyl		LC	1	0.031		0.2
Cherries (1 Sample)						
California	1 (1)					
Boscalid		Both	1	0.001		1.7
Fenhexamid		GC	1	0.049		10
Iprodione		LC	1	0.003		20
Tebuconazole		Both	1	0.013		5
Chives (1 Sample; **1 Violation**)						
Connecticut	1 (1)					
Fipronil		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Metolachlor		**Both**	**1**	**0.008**	**No Tolerance**	**0**
Thiabendazole		**LC**	**1**	**0.001**	**No Tolerance**	**0**
Collards (1 Sample)						
South Carolina	1 (1)					
Dimethomorph		Both	1	0.800		2
Flubendiamide		LC	1	0.144		0.6
Corn, On Cobb (4 Samples)						
Connecticut	0 (4)					
Cucumbers (3 Samples; 2 Unknown)						
Connecticut	0 (1)					
Unknown	2 (2)					
Azoxystrobin		LC	1	0.001		0.3
Chlorothalonil		LC	2	0.038-0.050	0.044	5
Imidacloprid		LC	1	0.012		0.5
Eggplant (2 Samples; 1 Unknown)						
Connecticut	1 (1)					
Dimethomorph		LC	1	0.002		1.5
Unknown	1 (1)					
Chlorothalonil		LC	1	0.019		6
Ginger, Root (1 Sample; 1 Foreign)						
Foreign (China)	1 (1)					
Lindane		GC	1	0.018		0.5
Grapes (1 Sample; 1 Foreign)						
Foreign (Chile)	1 (1)					
Boscalid		LC	1	0.004		3.5
Imidacloprid		LC	1	0.016		1
Trifloxystrobin		Both	1	0.022		0.2

Kale (1 Sample)						
Connecticut	0 (1)					
Kiwi (1 Sample; 1 Foreign)						
Foreign (Chile)	1 (1)					
Fenhexamid		GC	1	0.052		15
Iprodione		LC	1	0.003		10
Methidathion		GC	1	0.031		0.1
Lettuce (4 Samples; 1 Foreign; 1 *Organic*; **1 Violation**)						
Connecticut	1 (2)					
Boscalid		LC	1	0.002		11
Imidacloprid		LC	1	0.002		3.5
Oxyfluorfen		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Foreign (Canada)	1 (1)					
Boscalid		LC	1	0.005		11
Organic (Minnesota)	1 (1)					
Boscalid		LC	1	0.055		11
DCPA (Dacthal)		GC	1	0.006		2
Imidacloprid		LC	1	0.001		3.5
Nectarines (1 Sample)						
Connecticut	1 (1)					
Boscalid		Both	1	0.055		1.7
Fenbuconazole		LC	1	0.008		1
Phosmet		LC	1	0.040		5
Papaya (1 Sample; 1 Foreign)						
Foreign, (Mexico)	1 (1)					
Azoxystrobin		Both	1	0.609		2
Peaches (7 Samples; **1 Violation**)						
Connecticut	7 (7)					
Boscalid		Both	4	0.002-0.386	0.172	1.7
Captan		GC	1	0.146		15
Carbaryl		LC	1	0.011		10
Carbendazim (Metabolite)		LC	2	0.015-0.041	0.028	none*
Chlorothalonil		LC	2	0.001-0.014	0.008	0.5
Endosulfan		GC	1	0.036		2
Fenbuconazole		Both	7	0.004-0.270	0.085	1
Fenhexamid		Both	1	0.122		10
Fenpropathrin		LC	1	0.010		1.4
Imidicloprid		LC	1	0.125		3
Malathion		Both	1	0.022		8
Pendimethalin		LC	1	0.001		0.1
Phosmet		LC	6	0.004-0.137	0.046	10
Propiconazole		LC	1	0.019		1
Thiacloprid		**LC**	**1**	**0.013**	**No Tolerance**	**0**
Thiophanate Methyl		LC	3	0.003-0.132	0.052	3
Pears (3 Samples; **1 Violation**)						
Connecticut	3 (3)					
Boscalid		Both	3	0.003-0.024	0.013	3
Carbendazim (Metabolite)		LC	1	0.002		none*

Cyhalothrin, *lambda*		Both	1	0.028		0.3
Fenbuconazole		**LC**	**1**	**0.003**	**No Tolerance**	**0**
Fenpyroximate		LC	1	0.043		0.4
Fenvalerate		Both	1	0.078		2
Phosmet		LC	3	0.002-0.190	0.071	10
Thiamethoxam		LC	2	0.004-0.005	0.005	0.2
Thiophanate Methyl		LC	2	0.013-0.122	0.068	3
Trifloxystrobin		LC	2	0.004-0.007	0.006	0.5
Peas (2 Samples; 1 Foreign)						
Connecticut	1 (1)					
Azoxystrobin		Both	1	0.122		3
Foreign (Guatemala)	1 (1)					
Carbaryl		LC	1	0.006		10
Diazinon		LC	1	0.004		0.5
Peppers (6 Samples; 1 *Organic*)						
Connecticut	2 (5)					
Acephate		LC	1	0.574		4
Chlorothalonil		LC	1	0.001		6
Mandipropamid		LC	1	0.003		1
Organic (Connecticut)	0 (1)					
Plums (1 Sample; **1 Violation**)						
Connecticut	1 (1)					
Boscalid		LC	1	0.004		1.7
Captan		GC	1	0.119		10
Carbendazim		LC	1	0.033		none*
Endosulfan		GC	1	0.018		2
Fenbuconazole		LC	1	0.018		1
Imidacloprid		LC	1	0.001		3
Indoxacarb		LC	1	0.002		0.9
Propiconazole		Both	1	0.057		1
Thiacloprid		**LC**	**1**	**0.009**	**No Tolerance**	**0**
Potatoes (3 Samples; 2 *Organic*)						
Connecticut	1 (1)					
DDE		GC	1	0.002		1
Organic Connecticut	0 (2)					
Raspberries (1 Sample)						
Connecticut	0 (1)					
Squash (7 Samples; 1 Unknown)						
Connecticut	5 (6)					
Boscalid		LC	1	0.005		1.6
Carbaryl		Both	1	0.020		3
Chlorothalonil		LC	1	0.015		5
DDE		GC	3	0.001-0.005	0.002	0.1
Endosulfan		GC	1	0.008		1
Imidacloprid		LC	1	0.002		0.5

Unknown	0 (1)					
Strawberries (19 Samples; 1 *Organic*; **1 Violation**)						
Connecticut	13 (17)					
Bifenthrin		GC	2	0.005-01013	0.054	3
Boscalid		Both	7	0.003-0.141	0.054	4.5
Captan		GC	2	0.051-8.620	4.336	20
Carbendazim (Metabolite)		LC	4	0.001-0.106	0.043	none*
Chlorpyrifos		LC	1	0.005		0.2
Cyprodinil		Both	11	0.004-0.090	0.027	5
Dacthal (DCPA)		GC	1	0.026		2
Endosulfan		GC	3	0.022-0.092	0.056	2
Etoxazole		Both	1	0.014		0.5
Fenhexamid		Both	7	0.006-0.355	0.086	3
Fenpropathrin		Both	5	0.002-0.060	0.013	2
Fludioxonil		LC	4	0.005-0.025	0.014	2
Imidacloprid		LC	2	0.002		0.5
Pendimethalin		LC	3	0.001-0.003	0.002	0.1
Phosmet		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Pyrimethanil		LC	1	0.037		3
Thiabendazole		LC	1	0.010		5
Thiophanate Methyl		LC	1	0.084		7
California	1 (1)					
Boscalid		Both	1	0.001		4.5
Cyprodinil		GC	1	0.019		5
Fludioxonil		LC	1	0.016		2
Malathion		Both	1	0.047		8
Myclobutanil		GC	1	0.043		0.5
Organic (California)	1 (1)					
Fenbuconazole		LC	1	0.008		0.3
Sweet Potatoes (1 Sample; 1 Unknown; **1 Violation**)						
Unknown	1 (1)					
Dichloran (DCNA)		GC	1	9.600		10
Dimethoate		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Imazalil		**LC**	**1**	**0.001**	**No Tolerance**	**0**
Permethrin		**Both**	**1**	**0.014**	**No Tolerance**	**0**
Thiabendazole		LC	1	0.003		0.05
Tomatoes (12 Samples; 1 Foreign; 1 *Organic*; 1 Unknown)						
Connecticut	9 (10)					
Boscalid		Both	1	0.086		1.2
Carbaryl		Both	3	0.006-0.874	0.403	5
Chlorothalonil		Both	6	0.007-0.180	0.092	5
Cymoxanil		LC	1	0.030		0.2
Dinotefuran		LC	1	0.012		1
Fenhexamid		GC	1	0.155		2
Fludioxonil		Both	1	0.095		0.5
Imidacloprid		LC	3	0.003-0.041	0.017	4
Trifloxystrobin		Both	1	0.050		0.5

Foreign, *Organic*					
(Mexico)	0 (1)				
Unknown	1 (1)				
Carbaryl		LC	1	0.001	5
Chlorothalonil		LC	1	0.144	5

none* -- There is no US tolerance for carbendazim. Carbendazim has been used as a standalone pesticide in the past; however it is also a metabolite of the insecticides Thiophanate methyl and benomyl both of which undergo rapid degradation in the field to carbendazim. When 'none' is used, it indicates that the commodity has a tolerance for either/both benomyl and/or Thiophanate methyl. Provided the level of carbendazim is below the tolerance level of these pesticides on the specific commodity of interest, it is not considered a violation. When '0' is used it indicates that the metabolite carbendazim is not allowed because there is no tolerance for benomyl or Thiophanate methyl on these commodities. For a more comprehensive discussion on this subject the reader is referred to Krol *et al*, 2007.

Table 2: Summary of Pesticides Found in Processed Fruits and Vegetables Sold in Connecticut in 2009.

Commodity / Origin / Pesticide	Samples with Residues (Total)	Found by LC, GC or Both	Number of Times Detected	Residue Range (ppm)	Average Residue (ppm)	EPA Tolerance (ppm)
Juices						
Apple Cider/Juice (25 Samples; 1 Foreign; 1 *Organic*; 3 Unknown; **1 Violation**)						
Connecticut	10 (11)					
Acetamiprid		LC	2	0.007-0.013	0.003	1
Azinphos Methyl		LC	1	0.001		1.5
Boscalid		Both	5	0.001-0.011	0.004	10
Carbendazim (Metabolite)		LC	7	0.008-0.146	0.050	none*
Diphenylamine		Both	1	0.005		10
Imidacloprid		LC	2	0.001-0.015	0.008	0.5
Indoxacarb		LC	2	0.002-0.010	0.006	1
Phosmet		Both	7	0.002-0.182	0.034	10
Thiabendazole		LC	1	0.001		12
Thiacloprid		LC	2	0.003-0.009	0.006	0.3
Preservatives	*0 (11)*	*No potassium sorbate or sodium benzoate found*				
Florida	1 (2)					
Acetamiprid		LC	1	0.007		1
Carbendazim (Metabolite)		LC	1	0.010		none*
Diphenylamine		LC	1	0.024		10
Phosmet		LC	1	0.002		10
Pyrimethanil		LC	1	0.092		14
Thiabendazole		LC	1	0.066		12
Thiacloprid		LC	1	0.001		0.3
Preservatives	*0 (2)*	*No potassium sorbate or sodium benzoate found*				
Massachusetts	2 (2)					
Acetamiprid		LC	1	0.005		1
Boscalid		LC	1	0.002		10
Carbaryl		LC	1	0.002		12
Carbendazim (Metabolite)		LC	1	0.053		none*
Phosmet		LC	2	0.002-0.005	0.003	10
Preservatives	*1 (2)*	*0.010% Potassium sorbate; no sodium benzoate found*				
Maine	1 (1)					
Boscalid		LC	1	0.002		10
Carbendazim (Metabolite)		LC	1	0.032		none*
Diphenylamine		Both	1	0.030		10
Fenhexamid		**GC**	**1**	**0.061**	**No Tolerance**	**0**
Phosmet		LC	1	0.002		10
Thiabendazole		Both	1	0.070		12
Preservatives	*1 (1)*	*0.125% Potassium Sorbate; 0.004% Sodium Benzoate found* ***Both Undeclared***				

New York	2 (2)					
	Acetamiprid	LC	1	0.019		1
	Boscalid	LC	1	0.002		10
	Carbendazim (Metabolite)	LC	1	0.084		none*
	Diphenylamine	LC	1	0.003		10
	Imidacloprid	LC	1	0.002		0.5
	Phosmet	LC	2	0.002-0.005	0.003	10
	Thiacloprid	LC	1	0.007		0.3
	Preservatives	*2 (2)*	*0.010-0.045% Potassium sorbate; no sodium benzoate found*			
Pennsylvania	1 (1)					
	Acetamiprid	LC	1	0.040		1
	Azinphos-Methyl	LC	1	0.004		1.5
	Carbendazim (Metabolite)	LC	1	0.084		none*
	Phosmet	LC	1	0.024		10
	Preservatives	*1 (1)*	*0.052% Potassium sorbate; no sodium benzoate found*			
Vermont	1 (1)					
	Carbaryl	LC	1	0.015		12
	Carbendazim (Metabolite)	LC	1	0.026		none*
	Preservatives	*1 (1)*	*0.091% Potassium sorbate; no sodium benzoate found*			
Foreign						
(China)	0 (1)					
Organic						
	Preservatives	*0 (1)*	*No potassium sorbate or sodium benzoate found*			
(Connecticut)	1 (1)					
	Carbendazim (Metabolite)	LC	1	0.017		none*
	Phosmet	LC	1	0.007		10
	Preservatives	*0 (1)*	*No potassium sorbate or sodium benzoate found*			
Unknown	3 (3)					
	Acetamiprid	LC	3	0.010-0.016	0.013	1
	Azinphos-Methyl	LC	1	0.001		1.5
	Boscalid	LC	2	0.001		10
	Carbaryl	LC	2	0.001-0.011	0.006	12
	Carbendazim (Metabolite)	LC	2	0.034-0.061	0.048	none*
	Cyprodinil	GC	1	0.008		0.1
	Diphenylamine	LC	2	0.004-0.008	0.006	10
	Phosmet	LC	3	0.003-0.007	0.005	10
	Thiabendazole	LC	1	0.042		12
	Thiacloprid	LC	2	0.003-0.005	0.004	0.3
	Thiophanate-Methyl	LC	1	0.096		2
	Preservatives	*2 (3)*	*0.018-0.042% Potassium sorbate; no sodium benzoate found*			

Water (1 Sample; 1 Unknown)

Unknown	0 (1)

Fruit & Vegetables, Frozen

Blueberries (1 Sample; 1 Foreign; 1 *Organic*)

(Canada)	0 (1)

Strawberries (2 Samples; 1 Foreign; 1 *Organic*; 1 Unknown)

California	1 (1)

Fenpropathrin		Both	1	0.039		2
Imidacloprid		LC	1	0.011		0.5
Metalaxyl		Both	1	0.036		10
Myclobutanil		GC	1	0.085		0.5
Thiabendazole		LC	1	0.002		5
Foreign, *Organic*						
(Unknown)	0 (1)					
Fruits and Vegetables, Packaged Fresh						
Arugula (1 Sample; 1 Foreign; 1 *Organic*)						
(France)	0 (1)					
Blueberries (1 Sample)						
Oregon	1 (1)					
Cyprodinil		GC		0.003		1
Carrots (2 Samples; 1 Unknown)						
California	1 (1)					
Linuron		Both	1	0.002		1
Unknown	1 (1)					
Azoxystrobin		LC	1	0.001		0.5
Chlorothalonil		LC	1	0.005		1
Linuron		Both	1	0.011		1
Metalaxyl		LC	1	0.001		0.5
Celery (1 Samples; 1 Foreign; **1 Violation**)						
Foreign						
(Canada)	1 (1)					
Carbaryl		LC	1	0.004		3
Chlorpyrifos		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Diazinon		LC	1	0.002		0.7
Endosulfan		GC	1	0.013		8
Pendimethain		**LC**	**1**	**0.001**	**No Tolerance**	**0**
Greens, Kale (1 Sample; 1 Unknown)						
Unknown	1 (1)					
Cypermethrin		GC	1	0.141		2
Dimethomorph		LC	1	0.002		2
Imidacloprid		LC	1	0.005		3.5
Greens, Mustard (1 Sample; 1 Unknown)						
Unknown	1 (1)					
Cypermethrin		GC	1	0.125		2
Imidacloprid		LC	1	0.001		3.5
Lettuce (3 Samples; 3 *Organic*; 2 Unknown)						
Organic						
California	0 (1)					
Unknown	1 (2)					
Imidacloprid		LC	1	0.001		3.5
Limes (1 Sample, 1 Foreign)						
Foreign (Mexico)	1 (1)					
Chlorpyrifos		LC	1	0.001		1
Imazalil		Both	1	0.161		10

Thiabendazole	Both	1	0.830	10
Mushrooms (2 Samples; 1 *Organic*)				
Pennsylvania 1 (1)				
Carbendazim	LC	1	0.005	none*
Chlorothalonil	GC	1	0.019	1
Cyromazine	LC	1	0.005	1
Thiabendazole	LC	1	0.003	40
Organic				
Pennsylvania 1 (1)				
Thiabendazole	LC	1	0.033	40
Peas, Snow (1 Sample; 1 Foreign)				
Foreign				
(Guatemala) 1 (1)				
Chlorothalonil	LC	1	0.007	5
Dimethoate	LC	1	0.049	2
Spinach (2 Samples; 1 *Organic*; 1 Unknown)				
Massachusetts 0 (1)				
Organic				
Unknown 0 (1)				
Squash (1 Sample)				
Massachusetts 1 (1)				
DDE	GC	1	0.002	0.1
Other				
Honey (1 Sample; 1 Foreign)				
Foreign (India) 0 (1)				

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none* -- There is no US tolerance for carbendazim. Carbendazim has been used as a standalone pesticide in the past; however it is also a metabolite of the insecticides Thiophanate methyl and benomyl both of which undergo rapid degradation in the field to carbendazim. When 'none' is used, it indicates that the commodity has a tolerance for either/both benomyl and/or Thiophanate methyl. Provided the level of carbendazim is below the tolerance level of these pesticides on the specific commodity of interest, it is not considered a violation. When '0' is used it indicates that the metabolite carbendazim is not allowed because there is no tolerance for benomyl or Thiophanate methyl on these commodities. For a more comprehensive discussion on this subject the reader is referred to Krol *et al*, 2007.