Pesticide Residues in Produce Sold in Connecticut in 2008

WALTER J. KROL, PH.D., BRIAN D. EITZER, PH.D., MARYJANE INCORVIA MATTINA, PH.D., AND TERRI ARSENAULT
Department of Analytical Chemistry

The Connecticut Agricultural Experiment Station
New Haven, CT

Technical Bulletin 3

February 2010

Pesticide Residues in Produce Sold in Connecticut in 2008

WALTER J. KROL, PH.D., BRIAN D. EITZER, PH.D., MARYJANE INCORVIA MATTINA, PH.D., AND TERRI ARSENAULT
Department of Analytical Chemistry

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, 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 findings of the 208 samples analyzed in the calendar year 2008 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. 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 constantly updated and available in the electronic Code of Federal Regulations (e-CFR, 2009). 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 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.

[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.**

METHODS

Sample Collection:

Samples of produce grown in Connecticut, other states, and foreign countries were collected at 75 different Connecticut 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. For samples of olive oil, a 3 g sample size was employed 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 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 Automated Mass spectral Deconvolution and Identification System (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/0.1N 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. 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 from aliquots retained from the original sample 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

The 2008 market basket survey examined 208 samples of fresh (122; 58.7%) and processed (86; 41.3%) produce samples for the presence of pesticide residues. The results of this study are summarized in Table 1, for fresh produce, and Table 2, for processed produce. Of the 208 samples tested, 68 (32.7%) contained no pesticide residues. A total of 405 pesticide residues were found on the remaining 140 (67.3%) of samples tested. These residues consisted of 56 different pesticide Active Ingredients (AI's). Of those samples containing pesticide residues, 127 (61.1 % of the total samples) contained permissible levels of pesticide residues (non-violative residues); thirteen (6.3% of the total samples) contained sixteen residues which were not allowed (violative residues). Of the violative samples four (3.3% of the total fresh samples) were on fresh and nine (10.5% of the total processed samples) were on processed produce. There were 28 (13.5%) samples of organically grown food tested as part of this survey. A total of thirteen pesticide residues consisting of eleven different AI's were found on six (21%) of the organically grown food samples tested. Two of the six organically grown samples were found to contain violative residues (no tolerance) of three individual AI's. 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 (USDA NOP, 2008).

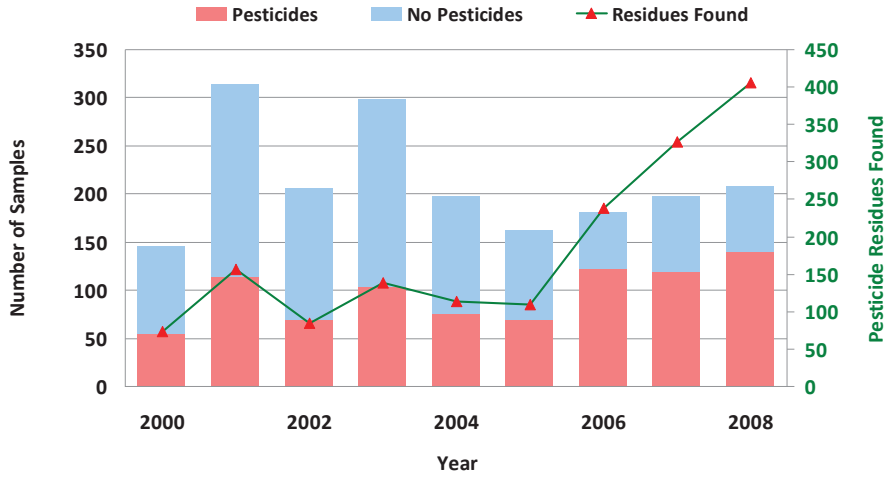
It should be noted that the CAES solely performs the analytical analysis of samples on behalf of the CT DCP, wherein regulatory authority lies. Enforcement actions (or lack thereof) taken by the DCP or the FDA are not always communicated back to the performing laboratories at the CAES. In those cases 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 on eight different commodities. There were twelve no tolerance violations and a single over tolerance violation (chlorpyrifos on pears). The violative processed samples were comprised of four pomegranate juices (2 foreign; 1 US; 1 unknown (unk)); two olive oils (1 foreign; 1 unk, organic); one black cherry drink (unk, organic); one sugar snap pea (foreign); one collard green (US). The fresh sample violations were comprised of one pear (foreign); one cucumber (foreign); and one each of cherry and lettuce grown in Connecticut.

The four samples of pomegranate juice all contained residues of the pesticide carbendazim (0.010-0.016 ppm). There are no US tolerances for carbendazim itself; however carbendazim is also a metabolite of the pesticides benomyl and thiophenate methyl, neither of which is allowed on pomegranate. A more complete discussion of this topic is provided in the 2007 pesticide residue bulletin (Krol et al, 2007). The results were forwarded to the DCP, and in turn to the FDA. As a result of these findings, the FDA issued a Class III nationwide recall of 6746 cases of this product (FDA Enforcement Report, 2008) on April 16, 2008. The olive oil samples were each found to contain violative residues of chlorpyrifos (0.004 & 0.006 ppm), and the one containing the higher level of chlorpyrifos, coincidentally labeled as 'organic', also contained phosmet (0.005 ppm). The findings were forwarded to the DCP and in turn to the FDA. No action was taken by the FDA because the levels detected by the CAES were below the current FDA detection levels in this matrix. The black cherry drink sample, also labeled as 'organic', was found to contain the pesticide thiabendazole (0.019 ppm) which is not allowed. A sample of frozen sugar snap peas from Guatemala contained residues of tebuconazole (0.098 ppm), imazalil (0.002 ppm) and carbendazim (0.080 ppm), all of which were violative. The CAES program has found similar violations in the past on fresh snap peas from Guatemala (Krol et al, 2006, 2007). A sample of frozen collard greens was found to contain violative residues of atrazine (0.001 ppm). This most likely occurred as plant uptake of atrazine residues present in the soil. In 2006 (Krol, 2006), we reported illegal residues of atrazine in spinach which was found to occur through plant uptake. Our findings led the EPA to establish a tolerance for atrazine on spinach; however this tolerance does not apply to collard greens in question. The results of the findings were forwarded to the DCP and in turn to the FDA for evaluation.

A sample of fresh pears from Argentina was found to contain illegal residues of chlorpyrifos (0.148 ppm). A sample of hydroponic cucumbers from Canada was found to contain illegal residues of cyprodinil (0.020 ppm). New York State also found illegal residues on this

Figure 1: Pesticide Residues in Food Sold in Connecticut 2000-2008.



product. The results of all analysis were forwarded to DCP and in turn FDA. No Federal recalls were issued. A sample of cherries grown in Connecticut was found to contain illegal residues of imazalil (0.002 ppm). A sample of lettuce grown in Connecticut was found to contain illegal residues of chlorothalonil (0.088 ppm). Letters were sent to the growers by the DCP notifying them of the violations.

A total of thirteen pesticide residues were found on six (21.4%) of the 28 samples of organically labeled produce samples. Three of these residues were contained on two violative samples as described above. The residues were found at concentrations of 0.003 – 0.038 ppm with an average of 0.014 ppm. The sample of black cherry drink accounted for six of the individual residues found. The remaining samples each contained one residue with the exception of an organic olive oil sample which contained two violative residues.

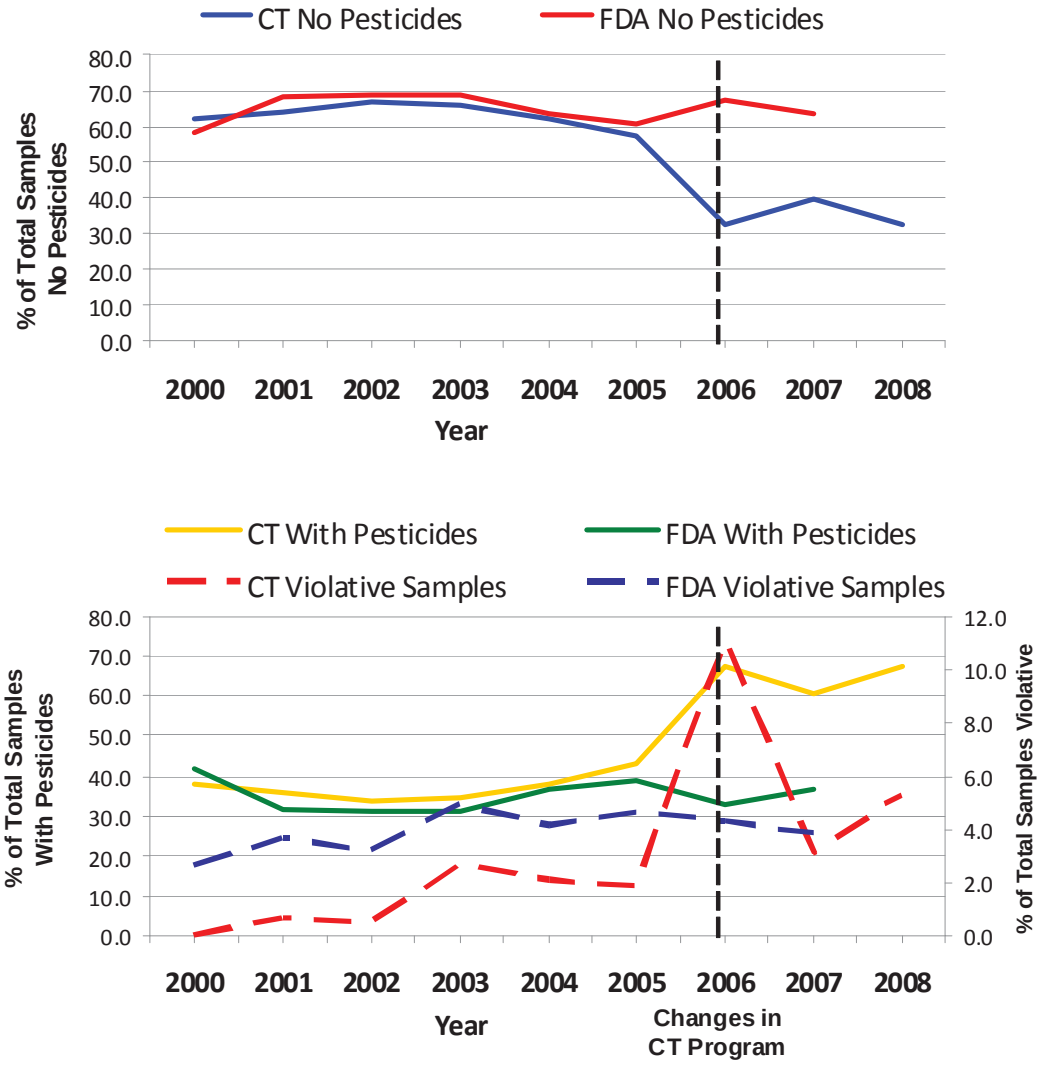
PROGRAM IMPROVEMENTS

Summary results of the CAES pesticide residue program from 2000 to present are presented in Figure 1. The discord in the pesticide residues found from 2006 — 2008 compared to the previous years (2000 — 2005) is the result of several major (and ongoing) improvements made in our program. As described in previous work (Krol *et al*; 2006, 2007) the QuEChERS method was introduced for sample extraction; lower concentrations of chemicals were detected through the acquisition of new instrumentation; extracts are analyzed by both liquid and gas chromatography; new active ingredient standards were obtained; liquid and gas chromatographic libraries were constructed containing these new analytes to aid in the analysis of extracts.

During the pre-QuEChERS period in our laboratories (1990 — 2005), on average 63.3% of the samples contained no detectable pesticides residues. These results correlated well with those of the FDA pesticide residue monitoring program since 1990 (FDA, 1993 — 2007), and are summarized (in part) in Figure 2. During this timeframe, there were, on average, 1.3 pesticide residues per sample containing residues. Since 2006, when the improvements to our program were initiated, on average 34.9% of the samples were found to contain no detectable pesticide residues and the average residue per sample which contained residues jumped to 2.5. The average percentage of samples from 1990 – 2005 found to be pesticide free was 63.3% for the Connecticut program and 64.5% for the Federal program. Figure 2 shows the relative percentages of pesticide free samples and those containing pesticide residues from 2000 – 2008 in the two programs. In 2006, the data in the Connecticut program diverged substantially from those in the Federal program owing to the improvements made in our laboratory.

It is important to note that the FDA has yet to implement the QuEChERS extraction protocol in the analysis of food products for pesticide residues. Our findings indicate that much less than half (~35%) of the samples offered for sale within the state are free from pesticide residues. The results presented by the FDA in 2006 and

Figure 2: Comparison of CT and FDA Results 2000-2008.



2007 may not truly represent the current market conditions in the US, as we feel that those reported by CAES do. This is highlighted by the violations reported by Connecticut to the FDA, which are below the current FDA detection limits, and thus resulted in no Federal recalls. The lower quantitation limits provided by the QuEChERS method calls into question what levels of pesticide residues should be reported. The CAES uses a lower limit of reporting of 0.001 ppm (1 ppb). This is an issue that needs to be reviewed and considered by the EPA.

CONCLUSIONS

In 2005, employing our older methods, a total of 109 pesticide residues were found in 70 (42.9%) of the samples examined; 57.1% of the samples were pesticide free. 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 the present work, 208 samples were examined for pesticide residues; 68 (32.7%) of which were found to contain no pesticide residues; 405 pesticide residues comprised of 56 different AI's were found on the remaining 140 (67.3%) of samples. Of the latter, 127 contained non-violative residues; thirteen samples contained sixteen violative residues. In samples containing residues, the average residue value was 0.087

ppm, and the average number of residues found on samples was 2.90. The current work supports our findings since 2006: that more of the produce sold in the marketplace contains pesticide residues than had been previously reported both in our studies prior to 2006 and those reported in the most recently published data of the FDA. The current work also confirms that the QuEChERS extraction protocol followed by GC/MS and LC/MS is more sensitive and, thus, superior to the methods used by CAES prior to 2006, and the FDA method (FDA, 1993 – 2007).

Our advances in extracting and analyzing pesticide residues have dramatically changed the outcome of our annual survey results over the past three years. Contrary to earlier work which showed that the majority of the samples analyzed (~63%) were free of pesticide residues, our advancements revealed that the majority of the samples in our survey, 65.1% since 2006, contained pesticide residues. Produce labeled as 'Organic' is not always free from pesticide residues. In 2008, 21.4% of the organic produce tested contained pesticides, compared to 12.5% in 2007, 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 tolerance limits. The average pesticide residue in 2008 was 0.087 ppm, and the average tolerance for those residues was 5.8 ppm (excluding violative samples). The average residue was 66.7 times 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

We would like to thank Ellen Sloan from the Food Division of the Department of Consumer Protection for providing samples for the market basket survey.

REFERENCES

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

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/

e-CFR [Electronic Code of Federal Regulations]. (**2008**) Title 40, Parts 180, 185, and 186. http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?&c=ecfr&tpl=/ecfrbrowse/Title40/40tab_02.tpl

FDA Enforcement Report for April 16, 2008. (**2008**) Available at: http://www.fda.gov/Safety/Recalls/EnforcementReports/2008/ucm120502.htm last accessed 01/16/2010.

FDA Pesticide Program Residue Monitoring: (**1993-2007**). http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Pesticides/ResidueMonitoringReports/default.htm

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

USDA NOP. (**2008**) Title 7, Chapter 1 (1-1-2008 Edition) §§ 205.671.

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

Table 1: Summary of Pesticides Found in Fresh Fruits and Vegetables Sold in Connecticut in 2008.

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 (24 Samples)						
Connecticut	19 (22)					
Acetamiprid		LC	2	0.001-0.003	0.002	1
Azinphos Methyl		LC	2	0.001-0.002	0.002	1.5
Boscalid		Both	9	0.001-0.217	0.046	10
Captan		GC	7	0.046-0.318	0.154	25
Carbaryl		Both	2	0.008-0.171	0.090	10
Carbendazim (Metabolite)		LC	6	0.002-0.043	0.022	none*
Cyprodinil		LC	2	0.002-0.003	0.003	0.15
Difenoconazole		LC	2	0.001-0.002	0.002	4.5
Diphenylamine		LC	1	0.003		10
Etoxazole		LC	1	0.002		0.5
Fenpropathrin		Both	2	0.004-0.021	0.021	5
Imidacloprid		LC	7	0.001-0.048	0.011	0.5
Indoxacarb		LC	1	0.002		3
Phosmet		Both	16	0.012-0.330	0.104	10
Pyriproxyfen		GC	1	0.058		0.8
Spirotetramat		LC	1	0.003		0.7
Thiacloprid		LC	3	0.005-0.014	0.008	0.6
Thiophanate Methyl		LC	8	0.001-0.116	0.118	2
Trifloxystrobin		Both	6	0.001-0.019	0.007	5
New York	1 (1)					
Azinphos Methyl		LC	1	0.002		1
Boscalid		Both	1	0.088		10
Captan		GC	1	0.237		25
Diphenylamine		Both	1	0.151		10
Thiabendazole		LC	1	0.012		12
Thiophanate Methyl		LC	1	0.093		2
Unknown Origin	1 (1)					
Acetamiprid		LC	1	0.002		1
Boscalid		LC	1	0.003		10
Diphenylamine		Both	1	0.160		10
Imidacloprid		LC	1	0.006		0.5
Phosmet		Both	1	0.065		10
Pyrimethanil		LC	1	0.648		12
Thiabendazole		Both	1	0.042		12
Beans, Green (1 Sample)						
Connecticut	1 (1)					
Chlorothalonil		Both	1	0.027		5
Beets, Greens or Root (2 Samples)						
Connecticut	2 (2)					

DDE		GC	2	0.002-0.004		0.1
Blueberries (4 Samples)						
Connecticut	3 (4)					
Boscalid		Both	2	0.020-0.075	0.046	6
Carbaryl		Both	1	0.088		10
Imidacloprid		LC	1	0.011		3.5
Phosmet		LC	2	0.003		10
Celery (4 Samples; 2 *Organic*)						
California	2 (2)					
Chlorothalonil		LC	2	0.043-0.126	0.085	15
Imidacloprid		LC	2	0.004		6
Linuron		LC	2	0.020-0.023	0.022	0.5
Malathion		Both	2	0.017-0.024	0.021	8
Propiconazole		LC	1	0.002		5
Organic						
California	0 (1)					
Massachusetts	0 (1)					
Cherries (2 Samples; **1 Violation****)						
Connecticut	1 (1)					
Boscalid		Both	1	0.031		1.7
Fenbuconazole		Both	1	0.088		1
Imidacloprid		LC	1	0.009		3
Imazalil**		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Phosmet		Both	1	0.042		10
Thiophanate Methyl		LC	1	0.046		20
Foreign (Chile)	1 (1)					
Imidacloprid		LC	1	0.001		3
Iprodione		Both	1	2.6		20
Corn (2 Samples)						
Connecticut	0 (2)					
Cucumbers (9 Samples; 2 Foreign; 1 *Organic*; **1 Violation****)						
Connecticut	3 (5)					
Chlorothalonil		Both	2	0.011-0.053	0.032	5
Carbendazim (Metabolite)		LC	1	0.002		none*
Endosulfan		GC	1	0.009		1
Florida	1 (1)					
Azoxystrobin		LC	1	0.002		0.3
Chlorothalonil		LC	1	0.012		5
Thiamethoxam		LC	1	0.058		0.2
Foreign (**Canada****, Mexico)	2 (2)					
Azoxystrobin		Both	1	0.092		0.3
Boscalid		Both	1	0.179		0.2
Carbendazim (Metabolite)		LC	1	0.012		none*
Cyprodinil**		**Both**	**1**	**0.020**	**No Tolerance**	**0**
Metalaxyl		LC	1	0.001		1
Thiamethoxam		LC	1	0.020		0.2
Organic						

Connecticut	0 (1)					
Eggplant (1 Sample; 1 *Organic)*						
Connecticut	0 (1)					
Lettuce (6 Samples; 1 *Organic*; **1 Violation****)						
Connecticut	3 (3)					
Chlorothalonil**		**LC**	**1**	**0.088**	**No Tolerance**	**0**
Imidacloprid		LC	2	0.018-0.021	0.020	3.5
Unknown Origin	2 (2)					
Cyhalothrin, *lambda*		GC	1	0.056		2
Dimethomorph		LC	1	0.004		10
Imidacloprid		LC	2	0.004-0.008	0.006	3.5
Iprodione		LC	2	0.001-0.003	0.002	25
Organic						
Connecticut	0 (1)					
Melon, Honeydew (1 Sample)						
California	0 (1)					
Oranges (2 Samples)						
California	1 (1)					
Imazalil		Both	1	0.968		10
Thiabendazole		Both	1	0.690		10
Pendimethalin		LC	1	0.002		0.1
Foreign (S. Africa)	1 (1)					
Imazalil		Both	1	1.500		10
Thiabendazole		Both	1	1.100		10
Methidathion		Both	1	0.074		4
Peaches (7 Samples)						
Connecticut	7 (7)					
Boscalid		Both	6	0.001-0.334	0.109	1.7
Captan		GC	2	0.102-0.188	0.145	15
Carbaryl		Both	3	0.004-0.204	0.106	10
Carbendazim (Metabolite)		LC	2	0.003-0.071	0.037	none*
Endosulfan		GC	3	0.016-0.067	0.037	2
Fenbuconazole		Both	4	0.018-0.169	0.088	1
Imidacloprid		LC	1	0.004		3
Phosmet		Both	6	0.015-0.294	0.129	10
Propiconazole		Both	1	0.064		1
Thiophanate Methyl		LC	3	0.076-0.333	0.181	3
Trifloxystrobin		GC	1	0.006		2
Pears (6 Samples; 1 Foreign; **1 Violation****)						
Connecticut	4 (4)					
Boscalid		LC	2	0.005-0.034	0.020	3
Carbendazim (Metabolite)		LC	3	0.006-0.043	0.018	none*
Clothianidin		LC	1	0.003		1
Fenhexamid		GC	1	0.050		10
Imidacloprid		LC	1	0.003		0.6
Indoxacarb		LC	1	0.009		0.2
Phosmet		Both	3	0.003-0.087	0.043	10
Trifloxystrobin		Both	2	0.006-0.008	0.007	0.5

Oregon	1 (1)							
Azinphos-Methyl	LC	1	0.003					1.5
Boscalid	LC	1	0.001					3
Captan	GC	1	0.043					25
Clothianidin	LC	1	0.003					1
Endosulfan	GC	1	0.008					2
Thiabendazole	Both	1	1.700					5
Foreign (Argentina)	1 (1)							
Azinphos-Methyl	LC	1	0.024					1.5
Bifenthrin	GC	1	0.014					0.5
Captan	GC	1	0.160					25
Carbendazim (Metabolite)	LC	1	0.006					none*
Chlorpyrifos**	**LC**	**1**	**0.148**	**Over Tolerance**				**0.05**
Cyhalothrin, *lambda*	GC	1	0.047					0.3
Peas (13 Samples; 1 Foreign)								
Connecticut	1 (2)							
Boscalid	LC	1	0.001					0.1
Foreign (Guatemala)	1 (1)							
Chlorothalonil	LC	1	0.036					5
Peppers (14 Samples; 3 *Organic*)								
Connecticut	1 (1)							
Acephate	LC	1	0.110					4
Methamidophos	LC	1	0.030					1
Organic								
Connecticut	0 (1)							
Other US	0 (2)							
Plums (1 Sample)								
Connecticut	1 (1)							
Fenbuconazole	LC	1	0.010					1
Propiconazole	LC	1	0.002					1
Phosmet	LC	1	0.009					5
Thiophanate-Methyl	LC	1	0.224					0.5
Potatoes (15 Samples)								
Idaho	3 (3)							
Azoxystrobin	LC	1	0.002					0.03
Carbendazim (Metabolite)	LC	1	0.001					none*
Chlorothalonil	LC	1	0.002					0.1
CIPC (Chlorpropham)	Both	3	0.153-2.674	0.998				30
DDE	GC	2	0.004					1
Imidacloprid	LC	3	0.004-0.024	0.035				0.4
Thiabendazole	LC	1	0.031					10
Maine	1 (1)							
Azoxystrobin	LC	1	0.001					0.03
CIPC (Chlorpropham)	Both	1	0.07					30
Metalaxyl	LC	1	0.001					4
Washington State	0 (1)							
Potatoes, Sweet (1 Sample)								
North Carolina	0 (1)							

Rutabaga (1 Sample; 1 Foreign)						
Canada	1 (1)					
Chlorpyrifos		Both	1	0.002		0.5
Squash (16 Samples; 3 *Organic*)						
Connecticut	6 (11)					
Boscalid		LC	1	0.004		4.5
Chlorothalonil		Both	4	0.004-0.086	0.056	5
Deltamethrin		LC	2	0.011-0.015	0.013	0.2
Dieldrin		GC	1	0.012		0.1
Endosulfan		GC	2	0.013-0.018	0.016	1
Georgia	1 (1)					
Chlorothalonil		LC	1	0.015		5
Imidacloprid		LC	1	0.091		0.5
Florida	0 (1)					
Organic						
Connecticut	0 (1)					
Florida	0 (1)					
Unknown	1 (1)					
Thiophanate Methyl		LC	1	0.003		1
Strawberries (10 Samples)						
Connecticut	8 (8)					
Azoxystrobin		Both	1	0.063		10
Bifenthrin		GC	1	0.015		3
Boscalid		Both	4	0.008-0.277	0.080	4.5
Captan		GC	4	0.066-0.305	0.151	20
Carbaryl		Both	2	0.003-0.228	0.131	10
Carbendazim (Metabolite)		LC	1	0.082		none*
Cyprodinil		Both	6	0.007-0.126	0.033	5
Endosulfan		GC	1	0.037		2
Etoxazole		Both	2	0.001-0.043	0.022	0.5
Fenhexamid		Both	2	0.017-0.089	0.033	3
Fenpropathrin		Both	5	0.002-0.027	0.019	2
Fludioxonil		Both	1	0.072		2
Imidacloprid		LC	1	0.001		0.5
Thiabendazole		Both	1	0.002		5
Florida	2 (2)					
Captan		GC	2	0.789-0.929	0.859	20
Boscalid		LC	1	0.003		4.5
Cyprodinil		Both	2	0.005-0.008	0.403	5
Fenhexamid		Both	2	0.107-0.155	0.131	3
Fludioxonil		Both	1	0.375		2
Metalaxyl		LC	2	0.004-0.008	0.006	10
Pyrimethanil		Both	1	0.145		3
Thiophanate Methyl		LC	1	0.159		7
Tomatoes (10 Samples; 1 Foreign; 1 *Organic*)						
Connecticut	5 (8)					
Azoxystrobin		Both	1	0.013		0.2
Chlorothalonil		Both	2	0.006-0.031	0.021	5

Deltamethrin	LC	1	0.013		0.2
Imidacloprid	LC	2	0.006-0.344	0.175	6
Foreign (Mexico) 1 (1)					
Imidacloprid	LC	1	0.001		6
Metalaxyl	LC	1	0.003		3
Thiophanate Methyl	LC	1	0.008		0.5
Organic					
(Connecticut) 0 (1)					

---

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 thiophenate 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 thiophenate 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 thiophenate 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 2008.

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 (16 Samples; 2 *Organic*)						
Connecticut	5 (5)					
Acetamiprid		LC	1	0.003		1
Carbendazim (Metabolite)		LC	4	0.024-0.057	0.038	none*
Diphenylamine		Both	1	0.012		10
Imidacloprid		LC	1	0.002		3
Phosmet		Both	2	0.003-0.039	0.015	10
Thiacloprid		LC	1	0.011		0.6
Florida	1 (1)					
Carbendazim (Metabolite)		LC	1	0.008		none*
Thiabendazole		LC	1	0.005		12
Massachusetts	2 (2)					
Acetamiprid		LC	1	0.015		1
Azinphos Methyl		LC	1	0.002		1.5
Carbendazim (Metabolite)		LC	2	0.002-0.033	0.018	none*
Phosmet		Both	1	0.003		10
Thiabendazole		LC	1	0.014		12
Thiacloprid		LC	1	0.009		0.6
New York	1 (1)					
Acetamiprid		LC	1	0.009		1
Carbendazim (Metabolite)		LC	1	0.051		none*
Phosmet		LC	1	0.015		10
Thiacloprid		LC	1	0.002		0.6
Ohio	2 (2)					
Acetamiprid		LC	2	0.004-0.023	0.014	1
Azinphos Methyl		LC	1	0.002		1.5
Carbendazim (Metabolite)		LC	2	0.008-0.042	0.025	none*
Diphenylamine		Both	1	0.013		10
Imidacloprid		LC	1	0.001		3
Phosmet		Both	1	0.002		10
Pyrimethanil		LC	1	0.007		12
Thiabendazole		Both	2	0.001-0.047	0.024	12
Foreign						
Chile	1 (1)					
Acetamiprid		LC	1	0.002		1
Thiabendazole		LC	1	0.025		12
Thiacloprid		LC	1	0.003		0.06
Unknown	2 (2)					
Acetamiprid		LC	1	0.004		1

Boscalid		LC	1	0.001		10
Carbendazim (Metabolite)		LC	2	0.001-0.008	0.005	none*
Thiabendazole		LC	1	0.004		12
Thiacloprid		LC	1	0.006		0.06
Organic						
Spain	0 (1)					
Vermont	0 (1)					
Blueberry (1 Sample)						
Unknown	1 (1)					
Carbaryl		LC	1	0.015		10
Carbendazim (Metabolite)		LC	1	0.011		none*
Imazalil		LC	1	0.001	Allowed as part of juice blend	
Iprodione		LC	1	0.005		15
Thiabendazole		LC	1	0.048	Allowed as part of juice blend	
Cherries (2 Samples; 1 Organic; **1 Violation****)						
Unknown	1 (1)					
Boscalid		LC	1	0.004		1.7
Organic (Unknown)	1 (1)					
Boscalid		Both	1	0.025		1.7
Carbaryl		Both	1	0.036		10
Carbendazim (Metabolite)		LC	1	0.038		none*
Imidacloprid		LC	1	0.024		3
Propiconazole		LC	1	0.002		1
Thiabendazole**		**LC**	**1**	**0.019**	**No Tolerance**	**0**
Thiamethoxam		LC	1	0.005		0.5
Cranberry (3 Samples; 2 *Organic*)						
Unknown	0 (1)					
Organic (Unknown)	1 (2)					
Carbendazim (Metabolite)		LC	1	0.003		none*
Currant (2 Samples; 1 *Organic*)						
Unknown	0 (1)					
Organic (Unknown)	1 (1)					
Pyrimethanil		LC	1	0.01	Allowed as part of juice blend	
Elderberry (1 Sample)						
Unknown	1 (1)					
Propiconazole		LC	1	0.002		1
Grape (2 Samples; 2 *Organic*)						
Organic						
(Spain, Unknown)	0 (2)					
Mango (1 Sample; Unk)	0 (1)					
Olive Oil (3 Samples; 1 *Organic*; **2 Violations****)						
Italy	1 (1)					
Chlorpyrifos**		**LC**	**1**	**0.004**	**No Tolerance**	**0**
Oxyfluorfen		LC	1	0.031		0.05
Organic (Italy)	1 (1)					
Chlorpyrifos**		**LC**	**1**	**0.006**	**No Tolerance**	**0**
Phosmet**		**LC**	**1**	**0.005**	**No Tolerance**	**0**
Unknown	0 (1)					

Pineapple (4 Samples)						
Hawaii	1 (1)					
Carbaryl		LC	1	0.021		2
Foreign (Philippines)	0 (2)					
Unknown	0 (1)					
Pomegranate (11 Samples; 1 *Organic*; **4 Violations****)						
Foreign						
Azerbaijan	0 (2)					
China	2 (2)					
Carbendazim (Metabolite)**		**LC**	**2**	**0.010-0.011**	**No Tolerance**	**0***
Turkey	0 (2)					
Organic (Unknown)	0 (1)					
Unknown	2 (4)					
Carbendazim (Metabolite)**		**LC**	**2**	**0.011-0.016**	**No Tolerance**	**0***
Fruit & Vegetables, Canned (14 Samples; 1 *Organic*)						
Apples (1 Sample; 1 *Organic*)						
Michigan	0 (1)					
Beans (2 Samples)						
United States	1 (2)					
Carbendazim (Metabolite)		LC	1	0.035		none*
Malathion		LC	1	0.004		8
Carrots (1 Sample)						
Canada	1 (1)					
Endosulfan		GC	1	0.010		0.2
Corn (1 Sample)						
United States	0 (1)					
Grapefruit (1 Sample)						
Swaziland	1 (1)					
Bromacil		LC	1	0.031		0.1
Mushroom (2 Samples)						
China	2 (2)					
Carbendazim (Metabolite)		LC	1	0.010		none*
Thiabendazole		LC	2	0.012-0.014	0.013	40
Oranges (1 Sample)						
China	1 (1)					
Carbendazim (Metabolite)		LC	1	0.008		none*
Peaches (2 Samples)						
Greece	1 (1)					
Carbendazim (Metabolite)		LC	1	0.008		none*
China	0 (1)					
Peas (1 Sample)						
Canada	0 (1)					
Potatoes (1 Sample)						
United States	1 (1)					
Boscalid		LC	1	0.001		0.05
CIPC (Chlorpropham)		Both	1	0.110		30
Thiamethoxam		LC	1	0.003		0.25

Spinach (1 Sample)						
Arkansas	1 (1)					
Azoxystrobin		LC	1	0.039		30
Imidacloprid		LC	1	0.131		3.5
Fruits and Vegetables, Packaged Fresh (5 Samples; 2 *Organic*)						
Beets (1 Sample; France)	0 (1)					
Peas (2 Samples; **1 Violation****)						
California	0 (1)					
Guatemala	1 (1)					
Azoxystrobin		LC	1	0.001		3
Carbendazim (Metabolite)**		**LC**	**1**	**0.080**	**No Tolerance**	**0***
Chlorothalonil		GC	1	0.033		5
Imazalil**		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Tebuconazole**		**Both**	**1**	**0.098**	**No Tolerance**	**0**
Spinach (2 Samples; 2 *Organic*)						
California, Unknown	0 (2)					
Fruits and Vegetables, Frozen (8 Samples; **1 Violation****)						
Beans (1 Sample)						
United States Unk	1 (1)					
Boscalid		Both	1	0.016		1.6
Broccoli (1 Sample)						
Mexico	1 (1)					
Imidacloprid		LC	1	0.002		3.5
Collard Greens (1 Sample; **1 Violation****)						
Unknown	1 (1)					
Azoxystrobin		Both	1	0.019		3
Atrazine**		**LC**	**1**	**0.001**	**No Tolerance**	**0**
Permethrin		Both	1	0.095		15
Corn (1 Sample)						
Unknown	0 (1)					
Okra (1 Sample)						
United States Unk	0 (1)					
Peas (2 Samples)						
United States Unk	1 (2)					
Dimethoate		LC	1	0.001		2
Spinach (1 Sample)						
Unknown	1 (1)					
Boscalid		LC	1	0.002		1
Cypermethrin, *zeta*-		GC	1	0.440		10
Baby Foods and Cereal (13 Samples; 2 *Organic*)						
Apples (6 Samples; 1 *Organic*)						
Argentina	1 (1)					
Carbendazim (Metabolite)		LC	1	0.002		none*
Chile / Germany	1 (1)					
Cyprodinil		GC	1	0.002		0.1

Organic						
Argentina	1 (1)					
Thiabendazole		GC	1	0.002		12
Unknown	3 (3)					
Carbendazim (Metabolite)		LC	2	0.001-0.005	0.003	none*
Thiacloprid		LC	2	0.003-0.005	0.004	0.6
Grapes (1 Sample; *Organic*)						
Argentina	0 (1)					
Pears (3 Samples)						
Argentina	2 (3)					
Acetamiprid		LC	2	0.001-0.016	0.009	1
Carbendazim (Metabolite)		LC	1	0.004		none*
Clothianidin		LC	2	0.001-0.002	0.002	1
Phenylphenol, *ortho*-		GC	2	0.027-0.031	0.029	25
Thiabendazole		Both	2	0.202-0.277	0.240	5
Cream of Wheat / Farina (3 Samples)						
United States Unk	0 (3)					

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 thiophenate 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 thiophenate 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 thiophenate methyl on these commodities. For a more comprehensive discussion on this subject the reader is referred to Krol *et al*, 2007.