Pesticide Residues in Produce Sold in Connecticut in 2011 with Concurrent Surveillance for Microbial Contamination

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

The Connecticut Agricultural Experiment Station (CAES), Department of Analytical Chemistry, 123 Huntington Street, New Haven, CT 06504

JOHN FONTANA, PH.D. (HCLD) ABB, STACEY KINNEY

Connecticut Department of Public Health (DPH), Katherine A. Kelley State Public Health Laboratory, 395 West Street, Rocky Hill, CT 06067

ELLEN SLOAN

Connecticut Department of Consumer Protection (DCP), Food and Standards Division, 165 Capitol Avenue, Hartford, CT 06106

The Connecticut Agricultural Experiment Station
New Haven, CT

Technical Bulletin 10 *December 2013*

Introduction:

The Department of Analytical Chemistry at the Connecticut Agricultural Experiment Station (CAES), has collaboratively conducted an annual market basket survey of produce sold in Connecticut for pesticide residues with the Connecticut (CT) Department of Consumer Protection (DCP), and published the findings, at least in part, since 1963 (Krol *et al.*, 2006). The goals of this program were and 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.

Enforcement of the Environmental Protection Agency, (EPA) mandated pesticide residue tolerances require both the Food and Drug Administration (FDA) and DCP to know the amount and the specific pesticide residues present in foodstuffs offered for sale[1]. In Connecticut, the DCP relies upon the analysis performed within the Department of Analytical Chemistry at the CAES to determine these in foods sold within the state. 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 and manufactured foods. In the current year, samples were obtained from 90 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, 2012).

Violations of the law occur when pesticides are not used in accordance with label registration and are: 1) applied in excessive amounts (over tolerance) or 2) when pesticides are accidentally or deliberately applied to crops on which they are not allowed (no tolerance). The results of the laboratory findings at the CAES are forwarded to the DCP for all samples submitted. When violations are found on crops grown within Connecticut, the DCP notifies both the grower and the Connecticut Department of Energy and Environmental Protection (DEEP) of the results. The DEEP may perform an audit of the grower's records to ensure proper pesticide use. The DCP may also, at its discretion, recall or destroy the violative commodity /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.

Our 2011 findings have been separated into two reports. During the course of testing fourteen fresh herb samples as part of an ongoing survey with the CT DPH (*vide infra*) an unexpectedly high rate of pesticide residue violations were discovered. This led to a more in depth and focused study on pesticides in herbs which is reported separately. The herb data was separated to avoid skewing the results of the 2011 market basket study. The current work contains solely the findings of 212 non herb samples. A separate manuscript entitled "A Targeted Study of Pesticide Residues in Herbs Sold in Connecticut 2011" (Krol *et al.*, in preparation) contains the findings of the fourteen fresh herb samples which led us to the investigation; seven additional fresh herb samples; and twenty-four additional dried herb samples for a total of 45 samples.

The targeted study above was the culmination of an interagency collaboration with the CT Department of Public Health (DPH) that was established in 2010 for the concurrent microbiological testing in selected samples for *Escherichia coli* (*E. coli*) O157:H7, Shiga Toxin-Producing *E.coli* (STEC), *Salmonella* species and *Listeria monocytogenes*. This selected concurrent testing continued in 2011 on a total of forty samples received from the DCP. The findings of twenty-six of these samples are reported in this bulletin and the remaining fourteen are reported in Krol *et al.*, in preparation.

[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.

The microbiological testing results presented in this survey were undertaken at the CT DPH lab in Hartford. In 2010, the DPH received a grant from the United States Department of Agriculture (USDA) Food Safety and Inspection Service (FSIS) to test food in the marketplace for potentially harmful pathogens linked to human illness. Part of this grant included working with the Department of Analytical Chemistry at the CAES in its capacity as a chemistry Cooperative Agreement Program (cCAP) laboratory in the FDA Food Emergency Response Network (FERN). Utilizing the collection and regulatory arm of the CT DCP as the lead agency, in 2010 a pilot study was undertaken in which samples of food collected in the marketplace would undergo concurrent pesticide residue *and* microbial analysis. This pilot study continued in 2011. The DCP provided the CAES and DPH with identical, split, samples of material for this purpose. Results from the latter two agencies were forwarded back to the DCP to enforce any violations which were found.

This dual mode of testing food offered for sale in Connecticut helps to ensure that the consumer is protected not only from the use of illegal pesticides in the sample, but also ensures that the samples are devoid of any bacterial contamination that might be present. In 2011 it served as an impetus for an in depth survey for the testing of fresh and dried herbs for illegal pesticide residues (Krol *et al.*, 2013). Unfortunately, the CT DPH FSIS CAP grant discontinued its support for this concurrent pesticide residue and microbiological surveillance project in 2011.

Methods

Sample Collection:

Samples of produce grown in Connecticut, other states, and foreign countries were collected at 90 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. Twenty-six (26) of the 212 samples in the current report were split upon collection by the DCP inspector. An additional fourteen (14) samples are reported in a separate manuscript (Krol et al., in preparation). In these cases the inspector delivered half of the sample to the DPH labs in Hartford for microbial testing, and the other half to the CAES labs in New Haven for pesticide residue analysis. As with the other samples in this survey, samples were collected without prior knowledge of pesticide application or potential microbial contamination.

A) Pesticide Methods:

i. 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, a commercial Waring® blender with an explosion proof motor or with a 3 quart robot coupe® food processor. 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.

ii. 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 °C. 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.

iii. 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. Two (2) microliter 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 1200 High Pressure Liquid Chromatograph (HPLC) equipped with a Zorbax® SB-C18 Rapid Resolution (2.1 mm x 50 mm, 1.8μ) column; 3μL injection volume; flow rate 0.45 mL/min; gradient flow 95% A (H_2O/0.1N HCOOH) to B (100% MeOH/0.1N HCOOH) over 15 min in several steps; hold 100% B for 7 min. The column eluent 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. Alternatively and usually concurrently, LC analyses were made employing a Thermo Scientific Exactive Orbitrap MS run by Thermo Xcalibur® version 2.1.0.1140 with ToxID® version 2.1.2. The software controlled the MS and the Agilent 1200 Series HPLC used for the chromatographic resolution. The HPLC was equipped with a Thermo Hypersil gold aQ column (2.1 mm x 100 mm x 2.1 μ); 2μL injection volume; flow rate 0.25 mL/min; column temperature 40 °C; gradient flow: initial 99% A (water with 0.1% formic acid), 1% B (acetonitrile with 1% formic acid), hold 1 min, 1-10 min 99% A to 5% A, hold 5 min, 15.1 – 21.5 min 99% A. The column eluent was interfaced to the MS. The mass resolution was set to 100,000 with balanced settings and an injection time of 20 milliseconds (ms). The mass range of 75 – 1500 atomic mass units (amu) was monitored.

iv. Detection Limit of Pesticide Residues

All pesticide residue levels are reported in parts per million (ppm) based upon the fact that the EPA tolerance levels are established using this convention. The CAES reports all pesticide residues which are confirmed by MS to an arbitrarily set lower limit of 0.001 ppm (one part per billion (ppb)). There are many pesticide residues seen below this level, especially using LC/MS, that are not included in this work. We are currently working to establish limits of detection (LOD) and limits of quantitation (LOQ) for individual pesticide Active Ingredients (AI's) as part of our laboratories accreditation program.

v. 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). Further proof of this was obtained in unpublished work conducted in our laboratory 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(s) 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. High resolution (four decimal) exact mass spectra are obtained, employing the Exactive MS, as confirmation of all violative residues.

B) Microbiological Methods

All samples were processed using the FDA's Bacteriological Analytical Manual (BAM, 8th Edition, Revision A, 1998). The twenty-six produce samples included in this report, and the fourteen herb samples reported elsewhere (Krol *et al.*, in preparation) collected by DCP were delivered to the DPH laboratory. Briefly, the samples were weighed out in 1:10 aliquots and soaked in a selective pre-enrichment media. Following this pre-enrichment incubation, a Polymerase Chain Reaction (PCR) screening method, using a DuPont Qualicon BAX® detection system, was performed targeting the presence of *Salmonella* spp., *E. coli* 0157:H7, and *Listeria monocytogenes* Deoxyribonucleic Acid (DNA). Simultaneously, conventional microbiology was performed on the enriched samples, which involved culture plating onto selective agars, Enzyme Linked Immunoassays (ELISA), biochemical and confirmation testing. All samples were streaked onto 1) Xylose lysine Deoxycholate (XLD) agar for isolation of *Salmonella* spp. colonies 2) MacConkey with Cefixime and Tellurite agar and MacConkey Sorbitol Agar for *E. coli* 0157:H7 and STEC colonies and 3) modified Oxford agar for suspect *Listeria* colonies. Any suspect colonies were further characterized using biochemical and confirmation testing. ELISA was performed for the confirmation of *Salmonella* spp. and STEC Following identification and confirmation; all isolates were sent for Pulsed-Field Gel Electrophoresis (PFGE) for DNA fingerprinting using the Centers for Disease Control (CDC) PulseNet protocol. The PFGE laboratory results were compared to the DNA fingerprints in both the local and national databases which contain images obtained from clinical, environmental and food isolates.

Results and Discussion

As part of the 2011 pesticide residue program, a total of 257 samples were tested. There were forty five herb samples tested which are reported separately (Krol *et al.*, in preparation)[2]. The current report focuses on 212 samples of fresh (138; 65.1%) and processed (74; 34.9%) foods. The findings of the combined pesticide residue and microbial surveillance survey are detailed in Table 1, for fresh, and Table 2 for processed foods. Those samples which underwent concurrent analysis for microbial contamination are specified in these tables as bacterial analysis and denoted using green text.

Of the 212 samples tested, 143 (67.5%) were found to contain residues of at least one pesticide while the remaining 69 (32.5%) were found to be free of any detectible residues. Pesticide residues were found in 96 (69.6%) of the 138 samples of fresh produce and 47 (63.5%) of the 74 samples of processed foods tested. A total of 543 pesticides comprised of 65 different AI's were found during the course of this work; 36 different AI's were determined by GC/MS and 60 by LC/MS. The number of residues and different AI's found in 2011 once again surpass those found in any other previous year of this study. Of those samples containing residues, 126 (59.4% of the total samples) contained permissible (non-violative) residues, and 17 (8.0% of the total samples) contained 19 residues which were not allowed (violative samples). Two of these samples were marketed as organic. Of the violative samples 12 (8.7% of the total fresh samples) were found on fresh and 5 (6.8% of the total processed food samples) on processed foods. Both organic violations were on processed food.

[2] The FDA/FCC became interested in pesticide residues in herbs in 2011 and are listed as collaborating authors in this report.

A total of twelve residues of eight different AI's were found on six (20.0%) of the thirty organically grown food samples tested as part of this survey. The levels of pesticide AI found ranged from 0.001 to 0.011 ppm with an average value of 0.004 ppm. Comparatively, from 2001 – 2005, before the introduction on QuEChERS, on average 13.5% of organic samples tested were found to contain residues at an average level of 0.082 ppm. From 2006 – 2010, employing the QuEChERS protocol, on average 23.3% of the samples tested were found to contain residues at an average residue level of 0.015 ppm.

Of the thirty organic samples tested, ten (33.3%) were fresh and twenty (66.7%) were processed. Only one fresh sample of spring mix was found to contain pesticide residues. The remaining residues were found on processed food. There were two violative samples. The first of these was a sample of shredded lettuce which contained residues of the herbicide pendimethalin (0.002 ppm). There is zero tolerance for pendimethalin on lettuce which results in a no tolerance violation. Additionally, since this sample was sold as organic, it was also found to be in violation of the National Organic Program (NOP) exclusion from sale provision specifically related to pesticide residue testing. The NOP provision, in general terms, states that pesticide residues are allowed on organic produce provided that the residues are at levels below five percent (5%) of the EPA tolerance for the specific residue on the specific crop[3] *(*NOP, 2004). The second of these violations was the finding of 2,6 dichlorobenzamide (0.010 ppm) in a sample of banana – beet – blueberry baby food. 2,6 Dichlorobenzamide has no tolerance on any of the commodities contained in this sample. It is, however, also a metabolite produced by the degradation of two other pesticides; dichlobenil and fluopicolide. The maximum allowable amount of dichlobenil on any of the commodities in the baby food is 0.100 ppm, and for fluopicolide 0.150. Because either of these pesticides may have been legally applied the metabolite, 2,6 dichlorobenzamide, is allowed to be present in this organically produced food, provided it is at no more that 5% of the tolerance of either pesticide. In this case the finding is 10% of the tolerance of dichlobenil and 6.7% the tolerance of fluopicolide, and its finding results in a violation of the NOP provision for organically labeled food. The results from these analyses were forwarded to the DCP, who in turn forwarded them to the United States Department of Agriculture (USDA) and the FDA (where applicable). The USDA maintains the responsibility for enforcing the NOP.

It should be noted that the results of all analysis performed at the CAES and DPH were forwarded to the DCP. The laboratories at the CAES solely perform the analytical analysis of samples on behalf of the DCP, wherein all regulatory authority lies. Enforcement actions (or lack thereof) taken by the DCP, FDA or the USDA are not always communicated back to the CAES. In those cases where CAES is made aware of the outcome (i.e. stop sale, recalls, etc.) details of such are provided in the text. Recalls made by the FDA are available at: http://www.fda.gov/Safety/Recalls/. As of this writing, a review of this website indicated that none of the violations in this work, related to pesticide residues in food, have led the FDA to issue a recall notice in its enforcement reports.

The remaining fifteen violative samples found were comprised of ten different commodities as can be seen in Tables 1 & 2. There were a total of 75 individual residues on these fifteen samples; seventeen of which were violative. All of the illegal residues found resulted in no tolerance violations.

[3] 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.' See also: Krol *et al.,* 2006 for a more comprehensive discussion of the NOP.

Five of these samples were of foreign origin; nine of US origin with six grown in Connecticut, and a single sample whose origin was unknown. Violations were found on fresh samples of beans (1 Georgia, 1 Guatemala), nectarines (1 CT), parsnips (1 Canada), pears (3 CT), peas (1 Guatemala), potatoes (1 CT), spinach (1 US unknown, 1 Canada) and tomatoes (1 CT). The remaining three violations were found on samples of apple cider (1 US unknown, 1 unknown) and lettuce (1 Canada).

The first violative green bean sample was from Georgia and found to contain residues of the chlorotriazine herbicide atrazine (0.001 ppm). Atrazine is widely used in the production of corn to control unwanted weeds. It is also persistent in the soil to which it is applied and based upon unpublished results obtained in these laboratories and others may persist from one growing season to another (see Krol *et al.*, 2006). The second green bean sample was from Guatemala and was found to contain residues of the fungicide difenoconazole (0.008 ppm). The results of these analyses were communicated to the DCP, and were in turn forwarded to the FDA.

A sample of nectarines grown in Connecticut was found to contain residues of the fungicide thiophanate methyl (0.032 ppm) in addition to four other legal residues. A sample of peaches grown by the same grower and obtained and tested at the same time contained similar residue levels of the same five pesticides. All five residues are allowed on peaches. It is likely that the grower applied the same mixture of pesticides to both the peaches and the nectarines.

A sample of parsnips grown in Canada was found to contain illegal residues of the pre-emergent herbicide pendimethalin (0.003 ppm) as well as four other legal pesticide residues (0.006 – 0.034 ppm). The results of these analyses were communicated to the DCP, and were in turn forwarded to the FDA.

Three samples of pears, all grown in Connecticut, were found to contain illegal residues of the fungicide fenbuconazole (0.003 – 0.035 ppm). Fenbuconazole has no tolerance on pears, yet it has a tolerance of 0.4 ppm on apples. No residues of fenbuconazole were found on apple samples obtained from the same three growers and tested at the same time. These applications were not likely due to the application of the same pesticide mix to apples and pears by these farmers. There was no Section 18 Action issued by the EPA (http://cfpub.epa.gov/oppref/section18/search.cfm) which might allow for limited emergency use of fenbuconazole on pears. It appears that these three growers all made misapplications of this fungicide to their pears.

A sample of shelled English peas from Guatemala was found to contain residues of carbendazim (0.006 ppm). Carbendazim is a fungicide in its own right, but has no tolerances in the US. It is also a metabolite of the fungicides benomyl and thiophanate methyl, neither of which is allowed for use on these commodities. The results of these analyses were communicated to the DCP, and were in turn forwarded to the FDA. We have reported several findings in the past of illegal residues found on snow peas from Guatemala (Krol et al. 2006 and 2007). The consumer should be aware that snow peas from Guatemala have a history of arriving to the US marketplace containing illegal pesticide residues.

A sample of Connecticut grown potatoes was found to contain residues of the phosphoramidothioate insecticide acephate (0.024 ppm) in addition to one other pesticide which was allowed.

Two separate samples of fresh spinach, one from Canada and one from an unknown location in the US, were found to contain two violative residues each. The sample of Canadian spinach was found to contain residues of the phenylurea herbicide diuron (0.018 ppm) and the methylthiotriazine herbicide prometryn (0.002 ppm). The sample of unknown US origin was found to contain the phenylurea herbicide linuron (0.003 ppm), and the preemergent herbicide pendimethalin (0.001). None of these herbicides is registered for use on spinach, resulting in two separate no tolerance violations. The results of these analyses were communicated to the DCP, and were in turn forwarded to the FDA.

A sample of tomatoes grown in Connecticut was found to contain residues of the carbamate fungicide thiophanate methyl (0.010 ppm). There is no tolerance for thiophanate methyl for any of the commodities in crop group 8 (fruiting vegetables), thus its finding resulted in a no tolerance violation.

There were two samples of apple cider of unknown origin which were found to contain separate residues of the insecticides dimethoate (0.002 ppm) and dinotefuran (0.003 ppm). Neither of these insecticides is allowed to be used in the production of apples. These findings resulted in two no tolerance violations. The results of these analyses were communicated to the DCP, and were in turn forwarded to the FDA.

The final violative sample in 2011 was a sample of chopped lettuce from Canada on which the herbicide pendimethalin (0.003 ppm) was found. Pendimethalin is not allowed for use in the production of the leafy vegetable group of crops, and its finding resulted in a no tolerance violation. The results of these analyses were communicated to the DCP, and were in turn forwarded to the FDA.

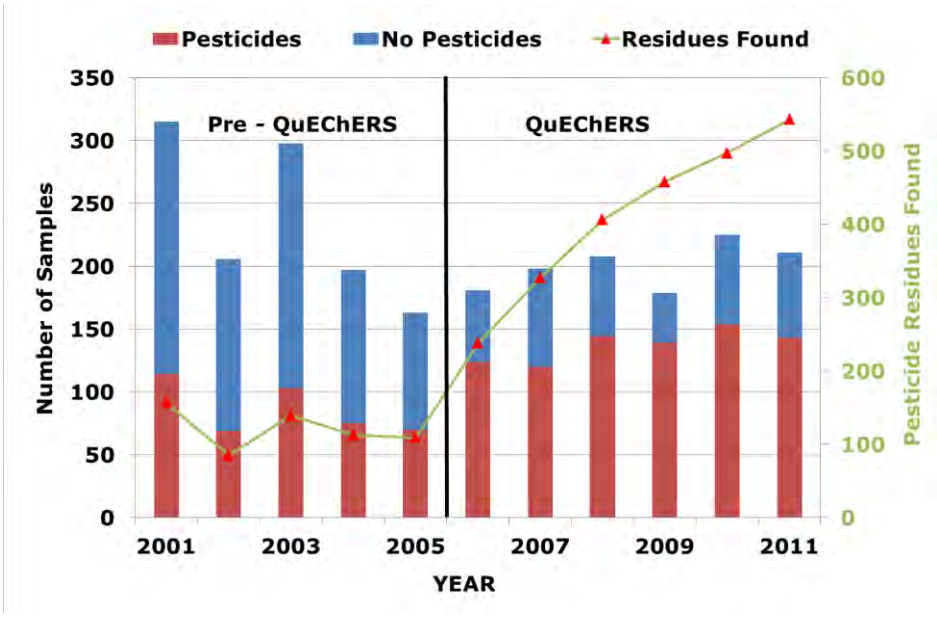
In addition to the pesticide analysis performed at the CAES we routinely perform analysis for potassium sorbate and sodium benzoate on samples of juices and ciders to help enforce labeling laws; these results are included in Table 2. These chemicals are routinely used in foods to preserve freshness by 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. 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). In 2011, a total of twenty six (26) samples were tested. Neither of these preservatives was found in any of the samples of carrot (2), orange (1) or quince (1) juice tested. Of the twenty two (22) apple juices and ciders tested, nine were found to contain potassium sorbate (0.024 – 0.04%) and none were found to contain sodium benzoate. In all cases where the potassium sorbate was found it had been appropriately declared as an additive on its label.

Program Improvements

Summary results of the CAES pesticide residue program from 2001 to 2011 are presented in Figure 1. A discernible change in the data is obvious in 2006 when we began screening for a larger number of pesticide AI's employing QuEChERS and employing LC/MS detection. The average number of samples containing pesticide residues increased from 36.6% (1179 samples; 431 with pesticides) pre QuEChERS (2001 – 2005) to 68.6% (1202 samples; 824 with pesticides) in the QuEChERS timeframe (2006 – 2011), and the average number of pesticide residues found per annum increased from 121 (603 total from 2001 – 2005) to 412 (2469 total from 2006 – 2011) (primary axis). The green line in Figure 1 (secondary axis) shows the change in the number of pesticide residues found each year over time. Since the program improvements in 2006, on average each year 61 additional residues from the previous year have been found. There were seventeen samples (8.0%) in which violative residues were found in 2011. In the pre-QuEChERS timeframe, on average, 1.5% (18 samples) of the samples tested was violative, and in the QuEChERS timeframe, on average, 6.9% (83 samples) were found to be violative.

The number of different AI's found on samples containing pesticides has increased from 1.4 in the pre-QuEChERS timeframe, to 3.0 in the QuEChERS timeframe. It should be observed that the results in all reports to date only include residues found above 0.001 ppm. This is an arbitrary lower limit set by the CAES for reporting. There are many instances in which pesticides are observed below this limit but are not reported. As part of our ongoing laboratory accreditation program we will be performing validation studies to obtain limits of detection (LOD's) and limits of quantification (LOQ's) for each individual pesticide AI studied.

Figure 1: Pesticide Residues in Food Sold in Connecticut 2001-2011.



From 1990 to 2005 the overall data of the CAES market basket program statistically matched those of the larger FDA pesticide residue monitoring program (Krol *et al.,* in press). Beginning in 2006, the CAES data was in marked contrast with those of the FDA. The data obtained from the CAES program correlate statistically with those of the USDA pesticide data program (PDP) (Krol *et al.,* in press). The FDA's sampling model more closely parallels the CAES model, and is representative over a larger range of commodities. The FDA program employs the older methods of pesticide analysis similar to those previously used at the CAES. The PDP program focuses on testing a large number of samples of a small group of commodities per year employing up to date methods of pesticide residue analysis.

Extension of the Program to Microbiological Testing

In 2010, the CT DPH joined the market basket survey and began concurrent testing of some of the produce collected by DCP for *E. coli* O157:H7, STEC, *Salmonella* spp. and *Listeria monocytogenes*. This active surveillance of produce was in response to a foodborne outbreak associated with alfalfa sprouts in 2010 and to an observed increase in outbreaks associated with other fresh produce. In 2011, the CT DPH added testing for the Shiga-toxin producing *E. coli* (STEC). In 2011 there were forty (40) separate food products collected as part of a continuation of the 2010 pilot study. Fourteen of these samples were fresh herbs and are reported on in a separate manuscript (Krol *et al.*, in preparation). The results included in Tables 1 and 2 of this report encompass the findings for the remaining twenty six samples of fresh fruits and vegetables which were of domestic (13), foreign (9) and unknown (4) origin. Of these twenty six samples tested, none was positive for bacterial contamination. A total of forty four pesticide residues were found on seventeen (65.4%) of the samples tested. Of these seventeen samples, five (19.2% of 26) were found to contain seven violative pesticide residues. These violative samples all contained residues on commodities where no tolerance exists, and all were of foreign or unknown origin. The violative samples were found on lettuce (2) which both contained residues of pendimethalin, peas (1) which contained residues of carbendazim, and spinach (2) which contained residues of pendimethalin, linuron, diuron and prometryn (*vide supra*).

The microbiological portion of this pilot study was funded by a grant from the United States Department of Agriculture (USDA) Food Safety and Inspection Service (FSIS). This pilot study came to an end in 2011 when the FDA FSIS instructed the CT DPH to focus on current capacity and capabilities and not on surveillance of non FSIS/USDA products. This pilot study had offered the opportunity to concurrently test for both residual pesticides and foodborne pathogens in produce that was consumed in CT. Additional funding to support ongoing simultaneous chemical and microbial surveillance is being sought.

Conclusions:

In the current work, once again, a greater number of AI's (65) and pesticide residues (543) were detected than in any other year in our survey. The vast majority of total residues found (526; 96.9%) were found to be within the tolerances set by the EPA. Of the 212 samples analyzed, 143 (67.5%) were found to contain pesticide residues. Residues were found in 69.6% of the fresh, 63.5% of the processed and 20.0% 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 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.

Of the 26 samples tested jointly for pesticide and microbial contamination, five samples (19.2%) contained violative pesticide residues. None of the samples reported here were found to contain microbial contamination, however one sample of chives, reported in a separate manuscript (Krol *et. al.*, in preparation) tested positive for *Listeria monocytogenes*. Whereas the focus of this program in the past has primarily been focused on pesticide residues, we look forward to restarting our joint testing efforts of food sold in CT for the inclusion of harmful microorganisms. Additional funding to support this ongoing simultaneous chemical and microbial surveillance is being sought. Microorganisms present in food, like pesticides, pose a risk to the consumer if inadvertently consumed. Unlike pesticides that we might consume, the health effects of unwanted microorganisms can prove to be of a more immediate health concern over a much wider geographic population.

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.

BAM 1998. Bacterial Analytical Manual, U. S. Food and Drug Administration, Department of Health and Human Services. Available online at: http://www.fda.gov/Food/ScienceResearch/LaboratoryMethods/BacteriologicalAnalyticalManualBAM/default.htm

e-CFR [Electronic Code of Federal Regulations]. 2012. Title 40, 24, Part 180. 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

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

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., Arsenault, T., White, J.C., Fontana, J., Kinney, A.S., Lin, L.A., Robinson, S., Sloan, E. A Targeted Study of Pesticide Residues in Herbs Sold in Connecticut 2011. In preparation.

Krol, W.J., Eitzer, B.D., Arsenault, T., Mattina, M.J.I., White, J.C. 2013. Significant Improvements in Pesticide Residue Analysis in Food Using the QuEChERS Method. *LC/GC North America* In press.

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.

US EPA section 18 actions searchable database http://cfpub.epa.gov/oppref/section18/search.cfm

Table 1: Summary of Pesticides Found in Fresh Fruits and Vegetables Sold in Connecticut in 2011.

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 (26 Samples; 1 *Organic*)						
Connecticut	24 (24)					
Acetamiprid		LC	4	0.004-0.064	0.035	1
Azinphos Methyl		LC	1	0.002		1.5
Boscalid		Both	13	0.002-0.144	0.041	3
Captan		GC	1	0.101		25
Carbaryl		LC	3	0.002-0.150	0.067	12
Carbendazim (Metabolite)		LC	13	0.010-0.100	0.049	none*
Chlorpyrifos		LC	1	0.002		0.01
Cyprodinil		Both	11	0.001-0.047	0.016	0.1
Difenoconazole		Both	10	0.001-0.032	0.009	1
Diphenylamine		Both	1	0.039		10
Fenbuconazole		GC	1	0.010		0.4
Fenpropathrin		Both	4	0.002-0.041	0.018	5
Fenpyroximate		LC	3	0.001-0.005	0.003	0.4
Imidacloprid		LC	6	0.001-0.018	0.006	0.5
Phosmet		Both	19	0.002-0.297	0.061	10
Pyraclostrobin		LC	10	0.003-0.031	0.015	8
Pyridaben		Both	3	0.002-0.025	0.011	0.75
Pyriproxyfen		Both	4	0.002-0.009	0.005	0.2
Thiamethoxam		LC	6	0.042-0.230	0.126	0.2
Thiacloprid		LC	7	0.001-0.038	0.017	0.3
Thiophanate Methyl		LC	4	0.042-0.230	0.126	2
Trifloxystrobin		Both	1	0.010		0.5
Washington	1 (1)					
Azinphos Methyl		LC	1	0.015		1.5
Boscalid		Both	1	0.010		3
Chlorantraniliprole		LC	1	0.013		1.2
Diphenylamine		Both	1	0.431		10
Fludioxonil		Both	1	0.175		5
Pyrimethanil		Both	1	0.052		14
Thiabendazole		Both	1	0.803		5
Organic (Washington)	0 (1)					
Asparagus (1 Sample)						
Connecticut	0 (1)					
Beans, Snap (6 Samples; 1 Foreign; 1 Unknown; **2 Violations**)						
Connecticut	1 (3)					
Carbaryl		LC	1	0.004		10
Metolachlor		LC	1	0.001		0.3
Georgia	1 (1)					
Atrazine		**LC**	**1**	**0.001**	**No Tolerance**	**0**

Azoxystrobin		LC	1	0.003		3
Carbendazim (Metabolite)		LC	1	0.002		none*
Foreign (Guatemala)	1 (1)					
Azoxystrobin		Both	1	0.008		3
Difenoconazole		**Both**	**1**	**0.009**	**No Tolerance**	**0**
Dimethoate		Both	1	0.234		2
Unknown	0 (1)					
Beets (1 Sample)						
Connecticut	0 (1)					
Blueberries (3 Samples; 1 Foreign)						
Connecticut	1 (1)					
Cyprodinil		Both	1	0.005		10
Fenhexamid		LC	1	0.037		20
Florida	0 (1)					
Foreign (Chile)	1 (1)					
2, 6 Dichlorobenzamide (Metabolite)						
		LC	1	0.024		none*
Carbendazim (Metabolite)		LC	1	0.028		none*
Fenhexamid		Both	1	0.111		20
Phosmet		LC	1	0.186		10
Broccoli (1 Sample)						
Connecticut	0 (1)					
Cabbage (1 Sample)						
Florida	0 (1)					
Cantaloupe (1 Sample; 1 Bacterial Analysis)						
Florida	0 (1)					
Cauliflower (1 Sample)						
California	1 (1)					
Acephate		LC	1	0.144		2
Corn (2 Samples)						
Connecticut	1 (1)					
Chlorothalonil		LC	1	0.081		1
Florida	0 (1)					
Cucumbers (6 Samples; 1 Foreign)						
Connecticut	3 (5)					
Endosulfan		GC	2	0.001-0.003	0.002	1
Thiamethoxam		LC	2	0.002-0.007	0.004	0.2
Foreign (Mexico)	1 (1)					
Cyazofamid		LC	1	0.006		0.1
Metalaxyl		LC	1	0.006		1
Eggplant (1 Sample; 1 Unknown)						
Unknown	1 (1)					
Chlorothalonil		LC	1	0.005		6
Imidacloprid		LC	1	0.003		1
Methamidophos (Metabolite)		LC	1	0.030		none*
Grapes (1 Sample; 1 Foreign)						
Foreign (Chile)	1 (1)					
Boscalid		LC	1	0.008		3.5

Imidacloprid		LC	1	0.363		1
Oxyfluorfen		LC	1	0.003		0.05
Greens (3 Samples)						
Connecticut						
Beets	0 (1)					
Mustard	1 (1)					
Boscalid		LC	1	0.002		3
Sorrel	0 (1)					
Lemons (1 Sample; 1 *Organic*)						
Organic (California)	0 (1)					
Lettuce (4 Samples; 1 Foreign; 1 *Organic*; 2 Bacterial Analysis)						
California	1 (1)					
Imidacloprid		LC	1	0.014		3.5
Mandipropamid		LC	1	0.002		20
Pyraclostrobin		LC	1	0.050		
Connecticut	1 (2)					
Dacthal (DCPA)		GC	1	0.060		2
Imidacloprid		LC	1	0.041		3.5
Methomyl		LC	1	0.022		5
Pyraclostrobin		LC	1	0.002		29
Foreign, *Organic,* (Mexico)	0 (1)					
Mushrooms (1 Sample)						
Pennsylvania	1 (1)					
Permethrin		GC	1	0.041		5
Thiabendazole		LC	1	0.339		40
Nectarines (1 Sample; **1 Violation**)						
Connecticut	1 (1)					
Boscalid		LC	1	0.011		3.5
Fenbuconazole		Both	1	0.058		1
Imidacloprid		LC	1	0.005		3
Pyraclostrobin		LC	1	0.005		2.5
Thiophanate Methyl		**LC**	**1**	**0.032**	**No Tolerance**	**0**
Okra (1 Sample)						
Connecticut	0 (1)					
Parsnips (2 Samples; 1 Foreign; **1 Violation**)						
Connecticut	1 (1)					
Carbaryl		LC	1	0.003		2
Chlorothalonil		LC	1	0.025		1
Linuron		LC	1	0.006		0.05
Pyraclostrobin		LC	1	0.075		0.4
Foreign (Canada)	1 (1)					
Chlorothalonil		LC	1	0.017		1
Diazinon		LC	1	0.007		0.5
Linuron		LC	1	0.034		0.05
Pendimethalin		**LC**	**1**	**0.003**	**No Tolerance**	**0**
Pyraclostrobin		LC	1	0.006		0.4

Peaches (7 Samples)

Connecticut 6 (6)					
Boscalid	Both	5	0.007-0.090	0.034	1
Carbaryl	Both	1	0.012		10
Fenbuconazole	Both	5	0.022-0.082	0.041	1
Fenpropathrin	Both	1	0.071		1.4
Fenpyroximate	LC	1	0.006		0.4
Imidacloprid	LC	2	0.005-0.022	0.014	3
Phosmet	LC	2	0.017-0.128	0.073	10
Pyraclostrobin	LC	5	0.005-0.027	0.013	2.5
Thiophanate Methyl	LC	4	0.016-0.140	0.054	3
Trifloxystrobin	LC	1	0.001		2
New Jersey 1 (1)					
Clothianadin	LC	1	0.029		0.8
Cyhalothrin, *lambda*	GC	1	0.010		0.5
Endosulfan	GC	1	0.009		2
Fenpropathrin	Both	1	0.066		1.4
Fludioxonil	Both	1	0.012		5
Permethrin	Both	1	0.141		1

Pears (8 Samples; 1 Foreign; **3 Violations**)

Connecticut 6 (6)					
Acetamiprid	LC	1	0.025		1
Bifenthrin	GC	1	0.148		0.5
Carbaryl	LC	1	0.002		12
Carbendazim (Metabolite)	LC	4	0.001-0.106	0.032	none*
Chlorpyrifos	LC	1	0.003		0.05
Cyhalothrin, *lambda*	GC	3	0.006-0.135	0.054	0.3
Cyprodinil	Both	3	0.010-0.111	0.050	0.1
Difenoconazole	Both	3	0.014-0.072	0.036	1
Diphenylamine	Both	1	0.065		5
Fenbuconazole	**LC**	**3**	**0.003-0.038**	**No Tolerance**	**0**
Fenpropathrin	Both	2	0.002-0.014	0.008	5
Fenpyroximate	LC	3	0.006-0.072	0.029	0.4
Imidacloprid	LC	1	0.008		0.5
Pendimethalin	Both	1	0.010		0.1
Permethrin	GC	1	0.046		0.05
Phosmet	LC	2	0.002-0.371	0.187	10
Pyridaben	Both	2	0.012-0.073	0.046	0.5
Thiacloprid	LC	1	0.007		0.3
Thiamethoxam	LC	2	0.001-0.006	0.004	0.2
Thiophanate Methyl	LC	1	0.194		0.5
Trifloxystrobin	Both	2	0.004-0.018	0.012	0.5
Washington 1 (1)					
Acetamiprid	LC	1	0.014		1
Etoxazole	LC	1	0.001		0.2
Fludioxonil	GC	1	0.172		5
Pyrimethanil	GC	1	0.756		14
Spirotetramat	LC	1	0.005		0.7

Thiophanate Methyl	LC	1	0.127		0.5
Foreign (Argentina) 1 (1)					
Methoxyfenozide	LC	1	0.052		1.5
Thiabendazole	GC	1	0.277		0.5
Peas (4 Samples; 3 Foreign; 1 *Organic*; **1 Violation**; 2 Bacterial Analysis)					
Connecticut 0 (1)					
Foreign (Guatemala) 2 (2)					
Azoxystrobin	Both	1	0.012		3
Carbendazim (Metabolite)	**LC**	**1**	**0.006**	**No Tolerance**	**0**
Chlorothalonil	LC	1	0.007		5
Organic (Guatemala) 0 (1)					
Peppers (7 Samples; 2 Foreign; 1 *Organic*; 1 Unknown)					
Connecticut 3 (3)					
Imidacloprid	LC	2	0.001-0.004	0.025	1
Foreign					
Honduras 1 (1)					
Acetamiprid	LC	1	0.031		0.2
Boscalid	Both	1	0.029		1.2
Carbaryl	LC	1	0.002		5
Imidacloprid	LC	1	0.043		1
Pyraclostrobin	LC	1	0.325		1.4
Spirotetramat	LC	1	0.004		2.5
Mexico 1 (1)					
Acephate	LC	1	0.180		4
Boscalid	LC	1	0.009		1.2
Carbaryl	LC	1	0.009		5
Chlorpyrifos	LC	1	0.005		1
Dimethoate	LC	1	0.002		2
Endosulfan	Both	1	0.011		2
Methamidophos	LC	1	0.093		1
Thiamethoxam	LC	1	0.009		0.25
Unknown 1 (1)					
Imidacloprid	LC	1	0.002		1
Metalaxyl	Both	1	0.051		1
Pendimethalin	LC	1	0.004		0.01
Organic (Connecticut) 0 (1)					
Potatoes (5 Samples; 1 Foreign; **1 Violation**)					
Connecticut 3 (3)					
Acephate	**LC**	**1**	**0.024**	**No Tolerance**	**0**
Boscalid	Both	1	0.004		0.05
Carbendazim	LC	1	0.004		none*
DDT & Metabolites	GC	1	0.012		1
Dimethoate	LC	1	0.002		0.5
Imidacloprid	LC	1	0.001		0.4
Phosmet	LC	1	0.010		0.1
Idaho 1 (1)					
Chlorpropham (CIPC)	Both	1	2.486		30
Imidacloprid	LC	1	0.062		0.4

Thiamethoxam		LC	1	0.001		0.25
Foreign (Canada)	1 (1)					
Chlorpropham		Both	1	0.813		30
Imidacloprid		LC	1	0.022		0.4
Raspberries (1 Sample)						
Connecticut	1 (1)					
Boscalid		LC	1	0.930		6
Captan		GC	1	0.235		25
Cymoxanil		LC	1	0.003		4
Cyprodinil		LC	1	0.019		10
Fenpropathrin		Both	1	0.009		3
Fludioxonil		LC	1	0.003		5
Pyraclostrobin		LC	1	0.720		4
Spinetoram		LC	1	0.002		0.7
Spinach (6 Samples; 1 Foreign; 1 *Organic*; 2 Unknown; **2 Violations**; 3 Bacterial Analysis)						
Connecticut	0 (2)					
Foreign (Canada)	1 (1)					
Atrazine		LC	1	0.016		0.25
Linuron		**LC**	**1**	**0.003**	**No Tolerance**	**0**
Pendimethalin		**LC**	**1**	**0.001**	**No Tolerance**	**0**
Organic						
(California)	0 (1)					
Unknown (US)	0 (1)					
Unknown (US)	1 (1)					
Diuron		**LC**	**1**	**0.018**	**No Tolerance**	**0**
Prometryn		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Mandipropamid		LC	1	0.001		20
Sprouts, Mixed (4 Samples; 1 *Organic*; 2 Unknown; 4 Bacterial Analysis)						
Alfalfa						
Pennsylvania	0 (1)					
Unknown (US)	0 (1)					
Organic						
(Pennsylvania)	0 (1)					
Bean						
Unknown (US)	0 (1)					
Squash (10 Samples; 1 Foreign)						
Connecticut	4 (9)					
Boscalid		LC	2	0.002		1.6
DDT & Metabolites		GC	1	0.012		0.1
Endosulfan		GC	1	0.004		1
Pyraclostrobin		LC	1	0.006		0.5
Foreign (Mexico)	1 (1)					
Endosulfan		GC	1	0.096		1
Flonicamid		Both	1	0.049		0.4
Imidacloprid		LC	1	0.020		0.5
Thiamethoxam		LC	1	0.003		0.2
Trifloxystrobin		Both	1	0.006		0.5

Strawberries (4 Samples; 1 Foreign)						
Connecticut	2 (2)					
2,6 Dichlorobenzamide (Metabolite)		LC	2	0.003-0.006	0.005	none*
Boscalid		LC	2	0.009-0.015	0.012	4.5
Cyprodinil		LC	1	0.004		5
Pyraclostrobin		LC	2	0.003-0.004	0.004	1.2
Florida	1 (1)					
Boscalid		Both	1	0.153		4.5
Carbendazim (Metabolite)		LC	1	0.427		none*
Pyraclostrobin		LC	1	0.030		1.2
Pyrimethanil		Both	1	0.132		3
Spinetoram		LC	1	0.002		1
Foreign (Canada)	1 (1)					
Azoxystrobin		GC	1	0.071		3
Fenhexamid		LC	1	0.010		3
Myclobutanil		Both	1	0.011		0.5
Quinoxyfen		LC	1	0.004		0.9
Sweet Potatoes (1 Sample)						
Connecticut	1 (1)					
Carbaryl		LC	1	0.005		0.2
Tomatoes (16 Samples; 4 Foreign; 2 Organic; 2 Unknown; **1 Violation**; 5 Bacterial Analysis)						
Connecticut	4 (8)					
Azoxystrobin		LC	1	0.003		0.2
Chlorothalonil		Both	3	0.007-0.033	0.019	5
Difenoconazole		LC	1	0.001		0.6
Thiophanate Methyl		**LC**	**1**	**0.010**	**No Tolerance**	**0**
Massachusetts	0 (1)					
Maryland	0 (1)					
Foreign (Canada)	1 (1)					
Myclobutanil		LC	1	0.024		0.3
Foreign (Mexico)	1 (1)					
Dinotefuran		LC	1	0.005		0.7
Flonicamid		Both	1	0.003		0.4
Foreign (Mexico)	2 (2)					
Imidacloprid		LC	1	0.050		1
Thiamethoxam		LC	1	0.009		0.25
Unknown (US)	0 (1)					
Unknown	1 (1)					
Thiamethoxam		LC	1	0.009		0.25
Watercress (1 Sample; 1 Unknown; 1 Bacterial Analysis)						
Unknown (US)	1 (1)					
Azoxystrobin		LC	1	0.004		3
Cyprodinil		Both	1	1.335		20
Fludioxonil		GC	1	0.247		7
Imidacloprid		LC	1	0.009		3.5

FRESH TOTALS: SAMPLES		138	
	WITH RESIDUES	96	(69.6%)
	VIOLATIVE SAMPLES	12	(8.7%)
	ORGANIC SAMPLES	9	
	ORGANIC VIOLATIVE	0	(0.0%)
	BACTERIAL ANALYSES	18	
TOTAL DIFFERENT ACTIVE INGREDIENTS FOUND:		62	
TOTAL NUMBER OF RESIDUES FOUND:		356	
TOTAL NUMBER OF VIOLATIVE RESIDUES FOUND:		14	(12.8%)

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 2011.

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)
Baby Food (13 Samples; 1 Foreign; 9 *Organic*; 12 Unknown; **1 Violation**)						
Apples (2 Samples; 1 *Organic*; 2 Unknown)						
Organic (Unknown)	0 (1)					
Unknown	1 (1)					
Carbendazim (Metabolite)		LC	1	0.018		none*
Thiacloprid		LC	1	0.003		0.3
Apricot/Sweet Potato (1 Sample; 1 *Organic*; 1 Unknown)						
Organic (Unknown)	0 (1)					
Banana/Beet/Blueberry (1 Sample; 1 *Organic*; 1 Unknown; **1 National Organic Program {NOP} Violation**)						
Organic (Unknown)	1 (1)					
2,6 Dichlorobenzamide (Metabolite)		**LC**	**1**	**0.010**		**0.1**
**** Residue Present at Greater than 5% of Tolerance ****						
Beans, Green (2 Samples; 1 *Organic*; 2 Unknown)						
Organic (Unknown)	1 (1)					
Imidacloprid		LC	1	0.001		4
Unknown	1 (1)					
Carbendazim (Metabolite)		LC	1	0.001		none*
Carrots (1 Sample; 1 Unknown)						
Unknown	1 (1)					
Boscalid		LC	1	0.004		1
Carbendazim (Metabolite)		LC	1	0.001		none*
Mango (1 Sample; 1 Foreign; 1 *Organic*)						
Organic, Foreign						
Canada	0 (1)					
Pear/Mango/Spinach (1 Sample; 1 *Organic*; 1 Unknown)						
Organic (Unknown)	0 (1)					
Pumpkin (1 Sample, 1 *Organic*; 1 Unknown)						
Organic (Unknown)	0 (1)					
Spinach (1 Sample; 1 *Organic*; 1 Unknown)						
Organic (Unknown)	0 (1)					
Sweet Potato (2 Samples; 1 *Organic*; 2 Unknown)						
Organic (Unknown)	0 (1)					
Unknown	0 (1)					
Fruits & Vegetables, Canned or Jarred (7 Samples; 3 Foreign)						
Apples, Sliced (1 Sample; 1 Foreign)						
Foreign (China)	1 (1)					
Carbendazim (Metabolite)		LC	1	0.028		none*
Asparagus (1 Sample)						

Michigan	0 (1)					
Papaya (1 Samples; 1 Foreign)						
Foreign (Peru)	1 (1)					
Chlorothalonil		Both	1	0.012		15
Pears (2 Samples; 1 Foreign)						
California	0 (1)					
Foreign (China)	1 (1)					
Carbendazim (Metabolite)		LC	1	0.016		none*
Peas, Sweet (2 Samples)						
California	0 (2)					

Fruits & Vegetables Chopped or Shredded (13 Samples; 3 Foreign; 2 *Organic*; 7 Unknown; **2 Violations**; 7 Bacterial Analysis)

Apples (1 Sample; 1 Unknown)						
Unknown (US)	1 (1)					
Acetamiprid		LC	1	0.005		1
Boscalid		LC	1	0.011		3
Diphenylamine		Both	1	0.171		10
Imidacloprid		LC	1	0.001		0.5
Pyraclostrobin		LC	1	0.035		1.5
Pyrimethanil		GC	1	0.007		14
Thiabendazole		Both	1	0.770		5
Thiacloprid		LC	1	0.009		10
Carrots (1 Sample; 1 Unknown; 1 Bacterial Analysis)						
Unknown (US)	1 (1)					
Boscalid		Both	1	0.025		1
Cyazofamid		LC	1	0.005		0.09
DDT & Metabolites		GC	1	0.004		3
Linuron		Both	1	0.006		1
Pendimethalin		LC	1	0.002		0.5
Greens, Collard (1 Sample; 1 Unknown)						
Unknown (US)	1 (1)					
Azoxystrobin		LC	1	0.059		3
Garlic (1 Sample; 1 Foreign)						
Foreign (China)	0 (1)					
Lettuce (9 Samples; 2 Foreign; 2 *Organic*; 4 Unknown; **2 Violations**; **1 NOP Violation**; 6 Bacterial Analysis)						
Florida	1 (3); 1 Bacterial Analysis No Pesticides Found					
Imidacloprid		LC	1	0.002		3.5
Linuron		LC	1	0.004		2
Foreign (Canada)	2 (2)					
Boscalid		Both	1	0.190		11
Cymoxanil		LC	1	0.002		19
Diazinon		LC	1	0.001		0.7
Imidacloprid		LC	2	0.009-0025	0.017	3.5
Mandipropamid		LC	1	0.154		20
Metalaxyl		Both	1	0.012		5
Pendimethalin (lettuce only)		**LC**	**1**	**0.003**	**No Tolerance**	**0**

Organic (Unknown) 2 (2)

Dimethoate	LC	1	0.004		2
Dimethomorph	LC	1	0.001		10
Linuron	LC	1	0.002		2
Mandipropamid	LC	1	0.004		20
Methomyl	LC	1	0.008		5
Pendimethalin (lettuce only)	**LC**	**1**	**0.002**	**No Tolerance**	**0**
**** Residue Present at Greater than 5% of Tolerance ****					
Pendimethalin (lettuce mix)	Both	1	0.003		0.1

Unknown (US) 2 (2); 1 Bacterial Analysis, 1 pesticide found

Acetamiprid	LC	1	0.006		3
Atrazine	Both	1	0.135		0.25
Flonicamid	Both	1	0.037		4
Mandipropamid	LC	1	0.063		20
Methomyl	LC	1	0.008		5
Spinetoram	LC	1	0.005		8

Spring Mix (1 Sample; 1 *Organic*; 1 Unknown; 1 Bacterial Analysis)

Organic, Unknown 1 (1)

Pendimethalin	LC	1	0.001		0.1
Mandipropamid	LC	1	0.011		20

Fruits & Vegetables, Frozen

Beans, Green (2 Samples; 1 *Organic*; 2 Unknown)

Unknown (US) 1 (1)

Acephate	Both	1	0.696		3
Azoxystrobin	LC	1	0.007		3
Carbendazim (Metabolite)	LC	1	0.013		none*
Tebuconazole	Both	1	0.080		0.1

Organic;
Unknown (US) 0 (1)

Blueberries (1 Sample; 1 Unknown)

Unknown (US) 1 (1)

Azoxystrobin	Both	1	0.064		5
Boscalid	LC	1	0.017		6
Imidacloprid	LC	1	0.011		3.5
Methomyl	LC	1	0.004		6
Pyraclostrobin	LC	1	0.093		4

Broccoli (1 Sample; 1 *Organic* ; 1 Unknown)

Organic, Unknown
(US) 0 (1)

Corn (1 Sample; 1 *Organic*; 1 Unknown)

Organic, Unknown
(US) 0 (1)

Peas (2 Sample; 1 *Organic*; 2 Unknown)

Unknown (US) 0 (1)

Organic;
Unknown (US) 0 (1)

Soybeans, 'Edamame' (2 Samples; 2 Foreign, 1 *Organic*)

Foreign (China)	0 (1)					
Organic (China)	0 (1)					

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

Organic, Foreign						
Argentina	1 (1)					
2,6 Dichlorobenzamide (Metabolite)		LC	1	0.010		0.1
Unknown (US)	1 (1)					
2,6 Dichlorobenzamide (Metabolite)		LC	1	0.002-0.003	0.002	0.1
Boscalid		LC	1	0.002		4.5
Carbaryl		LC	1	0.027		4
Pyraclostrobin		LC	1	0.001		1.2

Juices/Ciders (29 Samples; 3 Foreign; 3 *Organic*; 9 Unknown; **2 Violations**)

Apple Cider/Juice (23 Samples; 1 Foreign; 1 Organic; 6 Unknown; **2 Violations**)

Connecticut	9 (9)					
Acetamiprid		LC	3	0.005-0.032	0.016	1
Azinphos Methyl		LC	1	0.011		1.5
Boscalid		LC	2	0.002-0.005	0.004	3
Carbaryl		LC	3	0.001-0.010	0.004	1.5
Carbendazim (Metabolite)		LC	9	0.001-0.116	0.037	none*
Cyprodinil		Both	2	0.002-0.004	0.003	0.1
Diazinon		GC	1	0.015		1.5
Diphenylamine		LC	1	0.006		30
Imidacloprid		LC	3	0.005-0.006	0.006	0.5
Phosmet		LC	7	0.001-0.009	0.004	10
Thiacloprid		LC	3	0.003-0.011	0.006	0.3
Thiamethoxam		LC	1	0.001		0.2
Preservatives	*2 (9)*	*(1) 0.035% potassium sorbate; (2) 0.002% sodium benzoate*				
Massachusetts	1 (1)					
Acetamiprid		LC	1	0.017		1
Boscalid		LC	1	0.004		3
Carbendazim (Metabolite)		LC	1	0.006		none*
Pyraclostrobin		LC	1	0.004		1.5
Preservatives	*1 (1)*	*0.025% potassium sorbate; no sodium benzoate found*				
New York	3 (3)					
Acetamiprid		LC	3	0.016-0.050	0.033	1
Boscalid		LC	1	0.001		3
Carbaryl		Both	1	0.005		1.5
Carbendazim (Metabolite)		LC	3	0.001-0.089	0.041	none*
Cyprodinil		Both	1	0.005		0.1
Diphenylamine		Both	1	0.034		30
Imidacloprid		LC	1	0.001		0.5
Phosmet		LC	1	0.009		10
Pyraclostrobin		LC	1	0.017		1.5
Thiacloprid		LC	3	0.002-0.006	0.004	0.3

Preservatives	*1 (3)*	*0.040% potassium sorbate; no sodium benzoate found*				
Pennsylvania	1 (2)					
Acetamiprid		LC	1	0.012		1
Carbaryl		LC	1	0.002		1.5
Carbendazim (Metabolite)		LC	1	0.053		none*
Chlorantraniliprole		LC	1	0.009		1.2
Cyprodinil		GC	1	0.001		0.1
Imidacloprid		LC	1	0.002		0.5
Methomyl		LC	1	0.001		1
Phosmet		LC	1	0.007		10
Thiacloprid		LC	1	0.004		0.3
Thiamethoxam		LC	1	0.001		0.2
Preservatives	*1 (2)*	*0.030% potassium sorbate; no sodium benzoate found*				
Foreign						
Argentina	1 (1)					
Acetamiprid		LC	1	0.001		1
Carbendazim (Metabolite)		LC	1	0.006		none*
Organic (Maine)	0 (1)					
Preservatives	*0 (1)*	*0.036% potassium sorbate found; no sodium benzoate found*				
Unknown (US)	5 (5)					
Acetamiprid		LC	3	0.014-0.018	0.016	1
Azinphos Methyl		LC	2	0.001		1.5
Boscalid		Both	3	0.004-0048	0.019	3
Carbaryl		LC	2	0.003		15
Carbendazim (Metabolite)		LC	5	0.005-0.157	0.055	none*
Chlorantraniliprole		LC	2	0.001-0.034	0.018	1.2
Dimethoate		**LC**	**1**	**0.002**	**No Tolerance**	**0**
Diphenylamine		Both	3	0.012-0.037	0.022	30
Flonicamid		LC	2	0.002		0.2
Imidacloprid		LC	1	0.001		0.5
Phosmet		LC	2	0.005-0.007	0.006	10
Pyraclostrobin		LC	2	0.001-0.004	0.003	8
Thiabendazole		Both	2	0.051-0.173	0.127	12
Thiacloprid		LC	2	0.002-0.003	0.003	0.3
Thiamethoxam		LC	1	0.001		0.2
Preservatives	*4 (5)*	*(1-4) 0.030% potassium sorbate; No sodium benzoate found*				
Unknown	1 (1)					
Acetamiprid		LC	1	0.012		1
Azinphos Methyl		LC	1	0.002		1.5
Boscalid		Both	1	0.003		3
Carbendazim (Metabolite)		LC	1	0.066		none*
Chlorantraniliprole		LC	1	0.017		1.2
Cyprodinil		GC	1	0.001		0.1
Dinotefuran		**LC**	**1**	**0.003**	**No Tolerance**	**0**
Fludioxonil		LC	1	0.021		5
Methomyl		LC	1	0.004		1
Phosmet		LC	1	0.006		10
Thiacloprid		LC	1	0.001		0.3

Thiamethoxam		LC	1	0.002	0.2
Preservatives	*1 (1)*	*0.024% potassium sorbate; No sodium benzoate found*			
Carrot Juice (2 Samples; 1 Organic; 2 Unknown)					
Unknown (US)	1 (1)				
Boscalid		Both	1	0.013	1
Linuron		LC	1	0.013	1
Metalaxyl		LC	1	0.001	0.5
Pyraclostrobin		LC	1	0.001	0.4
Organic					
Unknown (US)	0 (1)				
Preservatives	*0 (2)*	*No potassium sorbate or sodium benzoate found*			
Grape Juice (1 Sample; 1 Unknown)					
Unknown (US)	1 (1)				
Carbendazim (Metabolite)		LC	1	0.001	none*
Orange Juice (1 Sample, 1 *Organic*)					
Organic (Florida)	0 (1)				
Preservatives	*0 (1)*	*No potassium sorbate or sodium benzoate found*			
Pear Juice (1 Sample; 1 Foreign)					
Foreign (Argentina)	1 (1)				
Acetamiprid		LC	1	0.002	1
Carbendazim (Metabolite)		LC	1	0.002	none*
ortho-Phenylphenol		GC	1	0.007	25
Pyrimethanil		GC	1	0.015	14
Thiabendazole		GC	1	0.108	5
Thiacloprid		LC	1	0.002	0.3
Quince Juice (1 Sample, 1 Foreign)					
Foreign (Turkey)	0 (1)				
Preservatives	*0 (1)*	*No potassium sorbate or sodium benzoate found*			

PROCESSED TOTALS:	SAMPLES		74	
	WITH RESIDUES	47	(63.5%)	
	VIOLATIVE SAMPLES		5	(6.8%)
	ORGANIC SAMPLES		21	
	ORGANIC VIOLATIVE		1	(5.0%)
	BACTERIAL ANALYSES		8	
TOTAL DIFFERENT ACTIVE INGREDIENTS FOUND:		37		
TOTAL NUMBER OF RESIDUES FOUND:		187		
TOTAL NUMBER OF VIOLATIVE RESIDUES FOUND:		5	(2.7%)	

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.

FRESH TOTALS:	SAMPLES		138	
	WITH RESIDUES	96	(69.6%)	
	VIOLATIVE SAMPLES		12	(8.7%)
	ORGANIC SAMPLES		9	
	ORGANIC VIOLATIVE		0	(0.0%)
	BACTERIAL ANALYSES		18	
TOTAL DIFFERENT ACTIVE INGREDIENTS FOUND:		62		
TOTAL NUMBER OF RESIDUES FOUND:		356		
TOTAL NUMBER OF VIOLATIVE RESIDUES FOUND:		14	(12.8%) Of residues found	

PROCESSED TOTALS:	SAMPLES		74	
	WITH RESIDUES	47	(63.5%)	
	VIOLATIVE SAMPLES		5	(6.8%)
	ORGANIC SAMPLES		21	
	ORGANIC VIOLATIVE		1	(5.0%)
	BACTERIAL ANALYSES		8	
TOTAL DIFFERENT ACTIVE INGREDIENTS FOUND:		37		
TOTAL NUMBER OF RESIDUES FOUND:		187		
TOTAL NUMBER OF VIOLATIVE RESIDUES FOUND:		5	(2.7%) Of residues found	

FRESH AND PROCESSED				
SUM TOTALS:	SAMPLES		212	
	WITH RESIDUES	143	(67.5%)	
	VIOLATIVE SAMPLES		17	(8.0%)
	ORGANIC SAMPLES		29	
	ORGANIC VIOLATIVE		1	(3.4%)
	BACTERIAL ANALYSES		26	
TOTAL DIFFERENT ACTIVE INGREDIENTS FOUND:		66		
TOTAL NUMBER OF RESIDUES FOUND:		543		
TOTAL NUMBER OF VIOLATIVE RESIDUES FOUND:		19	(3.5%) Of residues found	

FRESH AND DRIED HERBS (See Krol *et al.*, in preparation)

SUM TOTALS:	SAMPLES		45	
	WITH RESIDUES	40	(88.9%)	
	VIOLATIVE SAMPLES		37	(82.2%)
	ORGANIC SAMPLES		3	
	ORGANIC VIOLATIVE		3	(100%)
	BACTERIAL ANALYSES		14	
TOTAL DIFFERENT ACTIVE INGREDIENTS FOUND:		60		
TOTAL NUMBER OF RESIDUES FOUND:		210		
TOTAL NUMBER OF VIOLATIVE RESIDUES FOUND:		165	(78.6%)	Of residues found

NOTES