

Food Safety Research in the Department of Analytical Chemistry: Surveillance of Fresh and Manufactured Foods for Chemical Contamination



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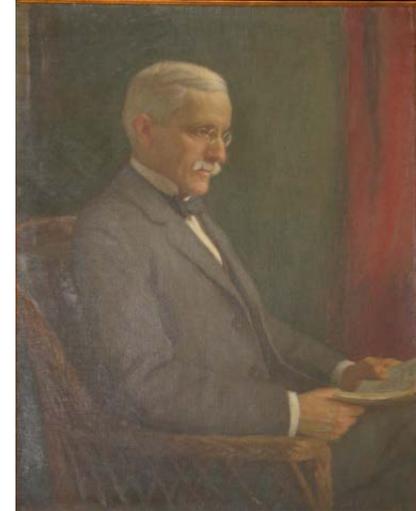
The Connecticut Agricultural Experiment Station



CAES and Food Safety

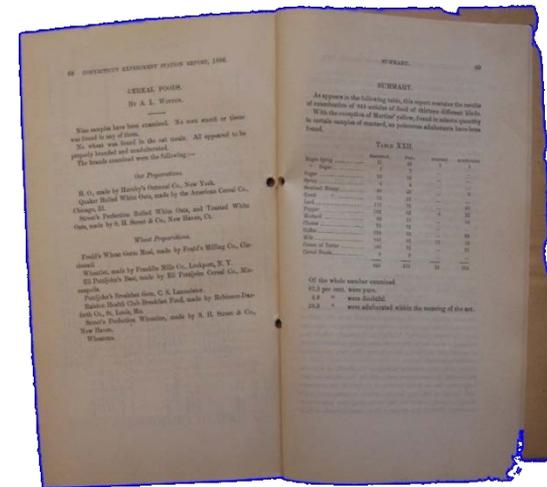
- The CAES was founded in 1875 with a \$2800 appropriation from the Legislature.
- The Experiment Station was to provide the Connecticut farmer with scientific information as required and to conduct experimental research in agriculture. The immediate focus was on the purity and safety of commercial fertilizers.
- In January 1895, a public act entitled “An Act Regulating the Manufacture and Sale of Food Products” was passed by the Legislature.
- Section 4 reads as “The Connecticut Agricultural Experiment Station shall make analysis of food products on sale in Connecticut suspected of being adulterated, at such times and places and to such extent...may take from any person...any article suspected of being adulterated...”

Samuel Johnson
First CAES Director



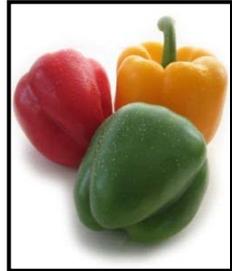
CAES and Food Safety

- The results of the first food safety study were published in 1896 and are available for viewing on our website (Bulletin 123)
- 848 food samples were analyzed; 14 broad categories
- 67% pure; 30% adulterated; 3% “doubtful”
- Commodities of greatest interest-
 - Maple syrup- 61 samples; 8 violations
 - Honey- 48 samples; 5 Violations
 - Coffee- 64 samples, 58 violations
- 50,595 food samples analyzed between 1896-1930



Part I: The Market Basket Survey

- Since 1964, CAES has conducted a Market Basket study with CT Department of Consumer Protection (DCP).
- Designed as a surveillance program for pesticide residues in the CT food supply; USDA Pesticide Data Program and FDA Pesticide Residue Monitoring Program have little or no presence in CT.
- In 2005, the Department was selected to join the FDA Food Emergency Response Network (FERN). We now routinely screen 200 food samples annually for hundreds of pesticides, as well as many toxins/poisons and other agents of concern for chemical terrorism.



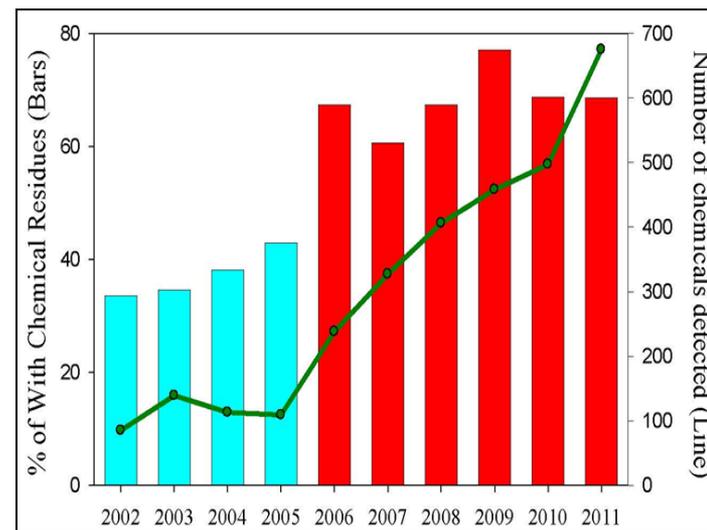
Part I: The Market Basket Survey

- As a result of the quality and robustness of our program, FDA and USDA do not sample CT food for pesticide residues.
- FERN supplies highly sensitive equipment for the chemical terrorism program; we are able to use that equipment for our state food safety program.
- DCP or FDA officials select commodities for analysis.
- Program expanded in 2010 with CT DPH for the simultaneous analysis for chemical residues and microbial pathogens.



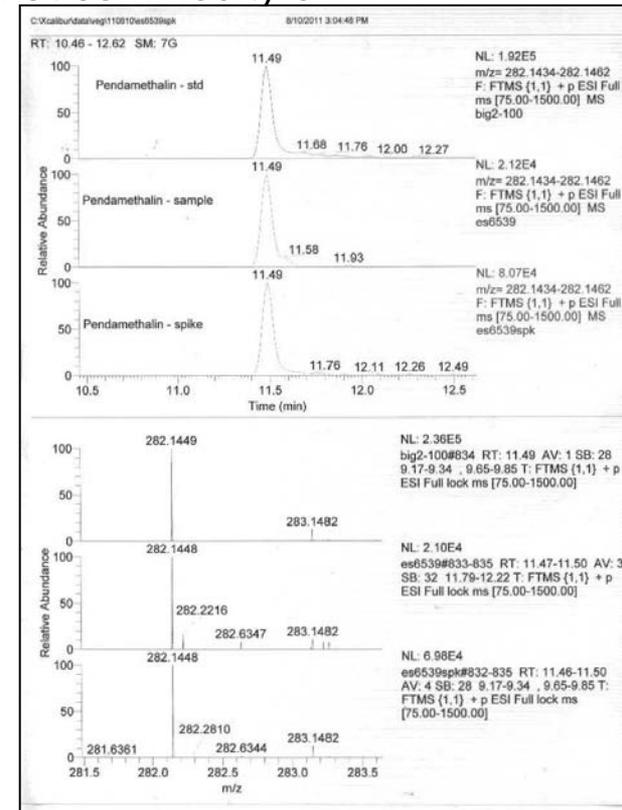
The Market Basket Survey- CAES Program Improvements

- In 2006, CAES switched to our current methods and now have much greater sensitivity.
- Pre-2006, 40% of samples contained residues. This agreed with FDA results. Since 2006, greater sensitivity has revealed 65% of foods have residues and a greater number of residue types are present. CT violation rates have doubled from 3-4% to 7-8% per year, depending on the commodities analyzed. FDA violation rates are in the 3-4% range.
- FDA routinely screens with GC-MS only. Most new residues are found by LC-MS.



The Market Basket Survey- Herbs

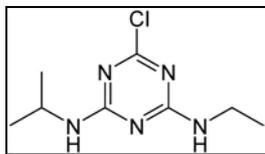
- Some pesticides are allowed in food
- Violations come in two flavors:
 - Residue found for which no EPA tolerance exists on that commodity or
 - Residue found above the EPA tolerance
- As part of the CAES-DPH project for pesticides/pathogens, DCP collected samples of fresh cilantro and parsley in January 2011.



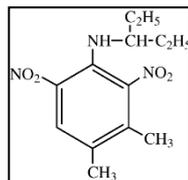
- The parsley had 6 residues but no violations
- The cilantro had 3 violative residues; none had tolerances (33 ppb acetamiprid [I], 21 ppb pendimethalin [H], and 8 ppb atrazine [H])



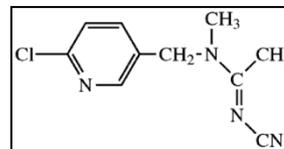
Atrazine



Pendimethalin

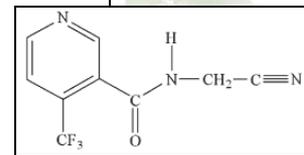


Acetamiprid



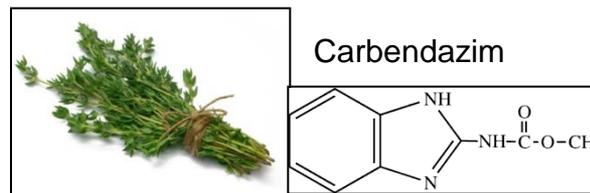
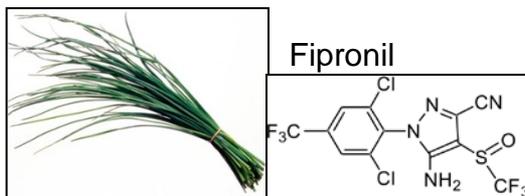
The Market Basket Survey-Herbs

- As a follow up and still as part of the CAES/DPH program on simultaneous surveillance for pesticides and pathogens:
 - **12** additional fresh samples were collected from May to July 2011 (tarragon, cilantro, chives, organic tarragon, basil, thyme, mint, and a blend)
 - All 12, including the organic tarragon, were violative. Over 25 different residues found.
 - The organic tarragon had 7 violative residues, including 1.5ppm cypermethrin (I) and 10ppm propinconazole (F)
 - One sample of chives had 5 violative residues, including 0.17ppm fipronil (I) and 0.68ppm carbendazim (F)
 - One sample of thyme had 5 violative residues, including 0.21ppm phosmet (I) and 16ppm carbendazim (F)
 - One blended sample containing thyme, rosemary, and parsley contained **13** violative pesticide residues, including 0.8ppm oxamyl (I), 0.31ppm pyraclostrobin (F), 0.30ppm cyromazine (I), and 0.28ppm flonicamid (I).



Flonicamid

➤ **RESIDUES AT THESE LEVELS ARE NOT AN IMMINENT PUBLIC HEALTH CONCERN**



USDA Pesticide Data Program

- Separately the USDA PDP collected 189 cilantro samples in May 2011; 44% contained violative residues. Chicago Tribune article on May 31, 2011 “USDA testing finds 30-plus unapproved pesticides on the herb cilantro”
- Herbs and spices are not commodities the USDA PDP, FDA Residue Monitoring Program or the CAES Market Basket survey have ever focused on.
- USDA/FDA go for commodities consumed in large quantities
- CAES goes for a cross-section of the market basket but haven't looked at these before




The Connecticut Agricultural Experiment Station
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ES6500B - SAMPLE REPORT - 7/11/11

Sample Number	Commodity	Reported Value (ppm)	Found	CFR Number	Tolerance (ppm)	Violation ??
ES6500B	Holiday Ham Blend (Thyme, Rosemary, Parsely)	0.104	Dinotefuran	40CFR180.603	0	YES
		0.076	Thiamethoxam	40CFR180.565	0	YES
		0.013	Clothianidin	40CFR180.586	0	YES
		0.005	Imidacloprid & Metabolites	40CFR180.472	48	NO
		0.049	Pronamide	40CFR180.317	0	YES
		0.01	Boscalid	40CFR180.589	0	YES
		0.01	Azoxystrobin	40CFR180.507	260	NO
		0.182	Profenofos	40CFR180.404	0	YES
		0.275	Fonicamid	40CFR180.613	0	YES
		0.203	2,6 Dichlorobenzamide	none see 231, 627	0	YES
			Dichlobenil*	40CFR180.231	0	YES
			Flupiclodide*	40CFR180.627	0	YES
		0.812	Oxamyl	40CFR180.303	0	YES
		0.342	Cyprodinil	40CFR180.532	170	NO
		0.025	Fludioxonil	40CFR180.516	65	NO
		0.305	Pyraclostrobin	40CFR180.582	0	YES
		0.1	Carbendazim	none 294, 371	0	YES
	Benomyl*	40CFR180.294	0	YES		
0.219	Flutriafol	40CFR180.371	0	YES		
0.295	Cyromazine	40CFR180.629	0	YES		
		40CFR180.414	0	YES		

*** Pesticides Listed in Red are Violations***

*Parent is a metabolite of these pesticides.
If these pesticides are allowed, the metabolite is also allowed.
Otherwise the finding of the metabolite is a violation.

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And the Dried Herbs?

- In August 2011, DCP Inspectors collected 24 dried herbs and spices, including basil, parsley, tarragon, cilantro, rosemary, thyme, chives, oregano. Two organic products collected.
- Manufacturers included Spice Classics, Nutmeg Spice, Gel Spice Co., McCormick, ...
- Of the 24 samples, 19 were violative; including organic parsley and thyme.
- Most residues in the ppb range
- Two separate dried parsley had 6 and 11 violative residues (11.6ppm methoxyfenozide [I])
- Two separate dried chives had 11 and 12 violative residues (3.3ppm thiophenate methyl [F])
- Dried tarragon contained 5 violative residues (10ppm propinconazole [F])




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9/21/11

ES6590 SAMPLE REPORT

Sample Number	Commodity	Reported Value (ppm)	Found	CFR Number	Tolerance (ppm)	Violation ??
ES6590	Chives, Dried	0.221	Acetamiprid	40CFR180.578	0	YES
		0.208	Imidacloprid & Metabolites	40CFR180.472	48	NO
		0.063	Carbofuran	40CFR180.264	0	YES
		0.023	Metaxyl	40CFR180.408	0	YES
		0.295	Dimethomorph	40CFR180.493	0	YES
		0.121	Difenoconazole	40CFR180.475	0	YES
		0.063	Chlorpyrifos	40CFR180.342	0	YES
		0.144	Acephate & Metabolites	40CFR180.108	0	YES
		3.700	Thiophenate Methyl & Metabolites	40CFR180.371	0	YES
		0.017	Methomyl	40CFR180.263	0	YES
		0.031	Oxadixyl	Revised 7/02 Effective 9/03	0	YES
		0.296	Iprodione	40CFR180.399	0	YES
		0.011	Propiconazole	40CFR180.434	0	YES
0.619	Pyrimethanil	40CFR180.518	0	YES		

VIOLATIONS ARE RED

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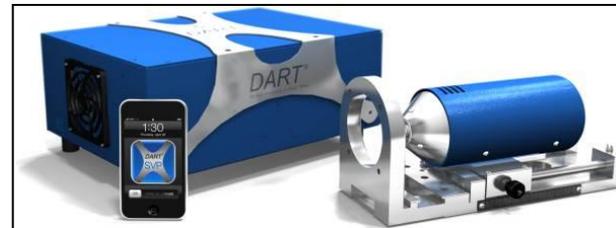
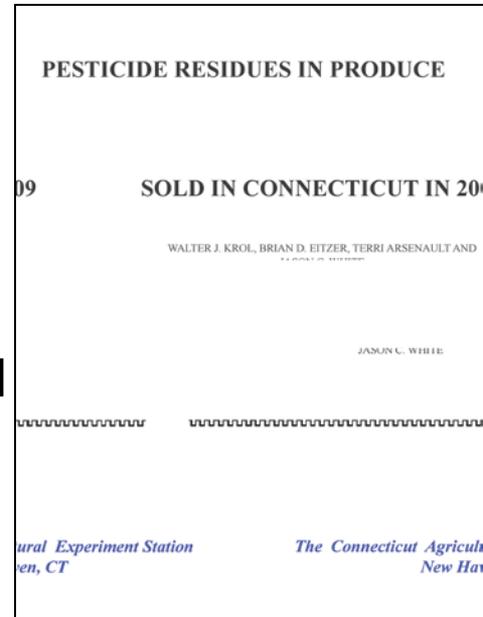
Regulatory Response

- We have tested 43 fresh and dried herbs; 35 have been violative. That is an 82% violation rate. Our normal rate is 7-8%;
- Except for the organic products (which fall to USDA), FDA has regulatory authority here (all grown outside CT; most in US)
- FDA is investigating but has noted that this is not a public health concern and they focus on “sample commodities of dietary importance such as foods consumed in large amounts by infants and children.”
- For the violations...
 - PPB levels (most of the residues) may be spray drift or incidental contamination.
 - PPM levels suggest direct and illegal application.



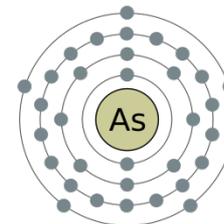
What is CAES doing?

- We publish our Market Basket report each year; for 2011 we will publish 2 reports (one on herbs specifically).
- We are working with the FDA Forensic Chemistry Center (FCC) to validate the DART (Direct Analysis in Real Time) on these herb samples. The DART is a field portable mass spectrometer with no chromatography.
- The DART is to be deployed with Customs and Border Protection to test food prior to entry into the country. This validation effort will also be written as a peer reviewed article (comparison of the DART to traditional extraction with LC-MS and GC-MS).



Part II: Arsenic in Apple Juice

- In September 2011, Dr. Oz drew criticism for a show focusing on the dangers of arsenic in apple juice.
- Dr. Oz hired an independent toxicology laboratory and found arsenic levels in some samples to be above the limit allowed in drinking water.
- The lab tested “dozens of samples” and found 10 samples over 10 ppb.
- A school district took apple juice off its menu after the show
- However, only total arsenic was measured; several forms of arsenic exist and some are considered harmless.
- There is no regulatory level for arsenic in juice. Focusing on 10ppb drinking water level is wrong; this is based on volume of water consumed (2-3 quarts per day).



What is Arsenic?

- Arsenic is a naturally occurring substance but can also result from contamination by human activity.
- There are two types of arsenic: organic and inorganic. The inorganic forms of arsenic are harmful, while the organic forms of arsenic are regarded as harmless.
- Because both forms of arsenic have been found in soil and ground water, small amounts may be found in certain food and beverages
- The FDA has been testing for arsenic in apple juice and other fruit juices for decades.
- The FDA has indicated that the vast majority of apple juice tested contains low levels of arsenic and is confident in the overall safety of apple juice consumed in this country.
- The maximum level of arsenic allowed in drinking water (including bottled) is 10 parts per billion (ppb).
- There is currently no regulatory level for arsenic in juice; the FDA is considering changing that policy. They have a level of concern (LOC) of 23 ppb.



Consumer Reports Follow Up



- The January 2012 Consumer Reports published an article entitled “Arsenic in your juice”
- 88 total samples of apple and grape juice were tested, including 19 different brands
- 90% of the samples were lower than 10 ppb total arsenic
- CR did have the samples speciated; “most” arsenic found was in the inorganic form
- Of 555 parents surveyed, 88% of children 5 and younger consumer less than 16 ounces (0.5 quarts).
- Remember the drinking water value for arsenic is based on 2-3 quarts per day.

Country-of-origin labeling (COOL)	Juice type (RTD = ready-to-drink package)	Package type	Size (fl. oz.)	Lot #	Total arsenic (ppb)	Total inorganic arsenic species (ppb) [1]	Total organic arsenic species (ppb) [1]	Total lead (ppb)
Turkey, Argentina, New Zealand	RTD	Plastic bottle	64	1	7.11	5.89	0.60	3.49
Argentina	RTD	Plastic bottle	64	2	7.00	6.74	0.71	3.79
China	RTD	Plastic bottle	64	1	1.67	1.03	0.55	1.40
China	RTD	Plastic bottle	64	2	4.37[2]	3.85[2]	0.94[2]	5.56[2]
China	RTD	Plastic bottle	64	3	1.37	0.60	0.51	0.50
USA, Argentina, China	RTD	Juice box(es)	8 x 6.75	1	5.02	2.49	1.88	2.05
USA, Argentina, China	RTD	Juice box(es)	8 x 6.75	2	5.30	3.06	2.23	3.44
USA, Argentina, China	RTD	Juice box(es)	8 x 6.75	3	10.5	4.13	4.85	1.90
Argentina	RTD	Plastic bottle(s)	4 x 4	1	9.69	10.48	0.92	13.6
Argentina	RTD	Plastic bottle(s)	4 x 4	2	8.66	7.65	0.88	7.08
Argentina	RTD	Plastic bottle(s)	4 x 4	3	5.82	3.48	0.69	3.41
Argentina	RTD	Plastic bottle(s)	4 x 4	1	5.74	4.44	0.90	2.21
Argentina	RTD	Plastic bottle(s)	4 x 4	2	5.68	4.55	0.95	2.28
Argentina	RTD	Plastic bottle(s)	4 x 4	3	5.47	3.89	0.78	2.23
China	RTD	Plastic bottle	64	1	3.14	2.05	0.69	2.87
China	RTD	Plastic bottle	64	2	9.38	4.99[3]	3.94[3]	5.57
China	RTD	Plastic bottle	64	3	8.56	5.44	3.61	4.84





From the FDA website March 2012

- This table represent some of the results from 94 samples of apple juice that were collected in late 2011
- Samples of various brands were collected
- The table displays test results for total arsenic, inorganic arsenic, dimethylarsinic acid (DMA) and monomethylarsinic acid (MMA).
- These results show that 95% of the samples tested below 10 ppb total arsenic; however, the arsenic found was predominantly in the inorganic form.
- The FDA has concluded that the very low levels detected during their surveillance are not a public health risk and the juice products are safe for consumption.

Sample ID	Total Arsenic Analysis*	Arsenic Speciation Analysis**		
	Total As Concentration (µg/kg, ppb)	Inorganic As Concentration (AsIII + AsV) (µg/kg, ppb)	DMA Concentration (µg/kg, ppb)	MMA Concentration (µg/kg, ppb)
561799	5.6	5.2	TR	0
561800	36	8.3	TR	19
592030	7.5	5.4	TR	0
606077	4.1	TR	TR	0
606078	6.6	3.9	0	0
615659	1.3	TR	0	0
629367	6.9	5.0	TR	0
629368	10	8.1	TR	0
645508	30	8.4	TR	20
645509	5.5	TR	0	TR
645510	1.4	TR	0	0
657385	TR	0	TR	0
658160	2.6	TR	0	0
658161	5.1	TR	0	0
658162	7.2	4.0	TR	TR



Next Steps

According to Michael R. Taylor, FDA's Deputy Commissioner for Foods...

- “Our test results over many years support the overall safety of apple juice,” says Taylor, “but we see a small percentage of individual samples tested that contain higher levels of arsenic.”
- “We want to minimize the public’s exposure to arsenic in foods as much as we can,” says Taylor. FDA plans to consider all the relevant evidence and, based on this work, may set a guidance or other maximum level to further reduce arsenic in apple juice and juice products.
- FDA is also taking the following actions:
 - Enhanced surveillance of arsenic in apple juice and juice concentrate. The agency will shortly have results for an additional 90 samples of apple juice and juice concentrate.
 - Continuing to test juice imported from China. The most recent results included more than 70 samples from China, and 95 percent contained less than the 10 ppb.
 - Enhanced surveillance on other types of juice, such as grape, pear, apricot,...Will involve FDA FERN Laboratories such as the CAES Department of Analytical Chemistry (FDA is buying CAES some new equipment for this work).
 - FDA has reached out to the juice industry to determine possible sources of arsenic





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