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

Jason C. White, Ph.D.
Department of Analytical Chemistry
The Connecticut Agricultural Experiment Station
CAES and Food Safety

- The CAES was founded in 1875 with a $2800 appropriation from the Legislature.
- The Station was to provide the CT farmer with scientific information and to conduct research in agriculture, with an immediate focus on fertilizer purity and safety.
- In January 1895, “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…”
CAES and Food Safety

- The results of the first food safety study were published in 1896 (Bulletin 123).
- 848 food samples were analyzed; 14 categories.
- 67% pure; 30% adulterated; 3% “doubtful.”
- Commodities of 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 the CT Department of Consumer Protection (DCP).

- Designed as a surveillance program for pesticide residues in the CT foods.

- In 2005, the Department was selected to join the FDA Food Emergency Response Network (FERN).

- We now screen 200+ food samples annually for pesticides, toxins/poisons and other agents of concern for chemical terrorism.
Part I: The Market Basket Survey

➢ As a result of the robustness of our program, the FDA and USDA do not sample CT foods for pesticides.

➢ FDA FERN supplies highly sensitive equipment for the chemical terrorism grant that we also use for our state program.

➢ DCP or FDA select foods for analysis.

➢ The program expanded in 2010 with CT Department of Public Health; simultaneous analysis for chemicals and bacteria.
The Market Basket - CAES Improvements

- In 2006, CAES switched to our current methods.
- Pre-2006, 40% of samples contained residues. 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.
Some pesticides are allowed in food.

Violations come in two flavors:

- Residue with no EPA tolerance.
- Residue above the EPA tolerance.

DCP collected fresh cilantro and parsley in January 2011.

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

CAES- Plant Science Day 2013

www.ct.gov/caes
As a follow up, 12 fresh samples were collected from May to July 2011.

All 12 had violations, including…

Organic tarragon with 7 violations: 1.5ppm cypermethrin (I) and 10ppm propinconazole (F).

Chives with 5 violations: 0.17ppm fipronil (I) and 0.68ppm carbendazim (F).

Thyme with 5 violations: 0.21ppm phosmet (I) and 16ppm carbendazim (F).

A blended sample contained 13 violations: 0.8ppm oxamyl (I), 0.31ppm pyraclostrobin (F), 0.30ppm cyromazine (I), and 0.28ppm flonicamid (I).

RESIDUES AT THESE LEVELS ARE NOT AN IMMINENT PUBLIC HEALTH CONCERN.
USDA Pesticide Data Program

- Separately the USDA collected 189 cilantro samples in May 2011; 44% contained violations. Chicago Tribune article on May 31, 2011 “USDA testing finds 30-plus unapproved pesticides on the herb cilantro.”
- Herbs/spices are not commodities the USDA, FDA or the CAES Market Basket survey have 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.
And the Dried Herbs?

- DCP collected 24 dried herbs/spices.
- Manufacturers included Spice Classics, Nutmeg Spice, Gel Spice Co., McCormick,...
- Of the 24, 19 had violations; including organic parsley and thyme.
- Residues were in the ppb range.
- Two dried parsleys had 6 and 11 violations (11.6ppm methoxyfenozoide [I]).
- Two dried chives had 11 and 12 violations (3.3ppm thiophenate methyl [F]).
- Dried tarragon contained 5 violations (10ppm propinconazole [F]).
Regulatory Response

- 43 fresh/dried herbs tested; 35 or 82% are violations. Our normal rate is 7-8%.

- FDA and USDA (organic foods) have regulatory authority (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…”

- For violations, ppb levels (most) may be spray drift or incidental contamination; ppm levels suggest direct application.
What is CAES doing?

- Our Market Basket report is published each year; for 2011 we will publish 2 reports (one on herbs).

- We are working with the FDA to validate the DART (Direct Analysis in Real Time) on these herb samples. The DART is a field portable mass spectrometer.

- The DART could be deployed with Customs and Border Protection to test food prior to entry into the country. This validation has been presented at scientific meetings.
Part II: Arsenic in Apple Juice

- In September 2011, Dr. Mehmet Oz drew criticism for a show focusing on the “dangers” of arsenic in apple juice.
- An independent laboratory found 10 samples over 10 ppb, the arsenic drinking water limit.
- Public response was strong; one school district took apple juice off its menu.
- However, only total arsenic was measured; several forms of arsenic exist and some are considered harmless.
- There was no regulatory level for arsenic in juice at the time. Focusing on the 10 ppb is problematic because it’s based on water consumption (2-3 quarts per day).
What is Arsenic?

- Arsenic occurs naturally but can also result from contamination by human activity.

- There are two types: organic and inorganic. Inorganic arsenic is harmful; organic arsenic is regarded as harmless.

- Both forms of arsenic found in soil and ground water; small amounts may be found in food/beverages.

- The FDA has been testing for arsenic in apple juice and other foods for decades.

- The vast majority of apple juice tested contains low arsenic levels; the FDA is confident in the overall safety of apple juice consumed in this country.
What is Arsenic?

- The maximum level allowed in drinking water is 10 ppb **total** arsenic.
- There was not a regulatory level for juice; there was a level of concern (LOC) of 23 ppb **inorganic** arsenic.
- **July 12, 2013** - The FDA has proposed creating an action level to 10 ppb **inorganic** arsenic.
January 2012 Consumer Reports- “Arsenic in your juice”

- 88 samples of apple and grape juice tested (19 brands)
- 90% were lower than 10 ppb total arsenic
- CR had the arsenic speciated; “most” was inorganic
- Of 555 parents surveyed, 88% of children consume less than 16 ounces/per day (0.5 quarts).
- The drinking water value for arsenic is based on 2-3 quarts per day.

### Table: Arsenic in Juice

<table>
<thead>
<tr>
<th>Country-of-origin labeling (COOL)</th>
<th>Juice type (RTO - ready-to-drink package)</th>
<th>Package type</th>
<th>Size (fl. oz.)</th>
<th>Lot #</th>
<th>Total arsenic (ppb)</th>
<th>Total inorganic arsenic species (ppb)</th>
<th>Total organic arsenic species (ppb)</th>
<th>Total lead (ppb)</th>
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</table>
FDA website- March 2012

- 94 apple juice samples (many brands) collected in late 2011
- Test results for total arsenic, inorganic arsenic, DMA and MMA.
- 95% of the samples tested below 10 ppb total arsenic; however, most was inorganic arsenic.
- The FDA has concluded that the very low levels detected are not a public health risk and the juice products are safe for consumption.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Total As Concentration (µg/kg, ppb)</th>
<th>Inorganic As Concentration (AsIII + AsV) (µg/kg, ppb)</th>
<th>DMA Concentration (µg/kg, ppb)</th>
<th>MMA Concentration (µg/kg, ppb)</th>
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Next Steps

- Establishing a new action level: 10ppb inorganic arsenic.
- Enhanced surveillance of apple juice. Results on the FDA website.
- Continue to test juice from China; 95% < 10ppb.
- Enhanced surveillance of other juices, such as grape, pear, apricot,…Involves FDA FERN Labs such as the CAES.
- Work with the juice industry to determine arsenic sources.
- Enhanced surveillance of arsenic in other foods (rice).
Arsenic Analysis in CT: ICP-MS

- FDA method: 40 minutes, 200°C microwave digestion in concentrated acid
- ICP-MS gives dozens of elements in 3 minutes
- Detecting 50 ppt (part per trillion!)
- The problem: ICP-MS only gives total arsenic
Analytical Issues: Total Arsenic

- We need arsenic species; not total arsenic
- **LC-ICP-MS** - It is still ICP-MS
- The LC allows separation of organic and inorganic species
- An extraction; dilute acid on a hot block at 90°C.
  - Separation first; each run is 22 minutes
  - Looks for arsenic only over the whole run

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$50,000  
$162,000  
$3,000
CT-FDA FERN Activities

- Running an FDA validation for arsenic species in food
- CT agencies (DoAg, DCP, DPH) also interested in arsenic in seaweed, rice, rice-based formula,…