Toxic Secrets

Pesticides uncovered in store brand cereal, applesauce, beans and produce

METHODS

This project is a collaborative effort of environmental, farmer, farmworker, consumer and beekeeper groups across the country. The following organizations submitted food samples: Beyond Toxics, CATA-El Comite de Apoyo a Los Trabajadores Agricolas, Ecology Center, Environment Texas, Emory University Turner Environmental Law Clinic, Friends of the Earth, Grassroots Environmental Education, Maryland Pesticide Education Network, Northwest Center for Alternatives to Pesticides, Ohio Ecological Food and Farm Association, People and Pollinators Action Network, Pesticide Action Network North America, Toxics Action Center and Toxic Free North Carolina.

Retailers and locations

Together, we shopped at 30 different stores in 15 states and we tested 132 samples of five different foods: apples, applesauce, spinach, oat cereal and pinto beans. We shopped at Walmart, Kroger, Costco and Albertsons/Safeway and their subsidiaries and we purchased house brand foods whenever possible. We only purchased non-organic (i.e., conventional) products. Samples were analyzed at Health Research Institute Laboratories. Oat cereal and pinto bean samples were tested for glyphosate. Apples, applesauce and spinach samples were tested for neonicotinoids.

Retailer	**Where we shopped**	**Subsidiaries**
Walmart	GA, MD, MI, OH, PA, MA, NY, MN	
Kroger	GA, MI, NC, OH, OR, CO, VA	• Baker's Supermarkets • City Market • Dillons Food Store • Fry's Food and Drug • Gerbes Super Markets • Harris Teeter • Jay C Food Stores • King Soopers • Kroger • Owen's • Pay Less Super Markets • QFC • Ralphs • Pick 'n Save • Mariano's Fresh Market • Metro Market • Copps • Scott's • Smith's • Fred Meyer • Foods Co. • Ruler Foods

Costco	CA, NC, OR, TX, WA, NY, MN	
Albertsons /Safeway	CA, MD, NJ, TX, WA, CO, VA, MA	• Acme • Albertsons • Amigos • Carrs • Haggen • Jewel-Osco • Lucky • Market Street • Pak 'n Save • Pavillions • Randall's • Safeway • Shaw's Super Saver Foods • Tom Thumb • United Supermarkets • Vons

Pesticides tested

Kind of pesticide	**Chemical we tested**	**Pesticide(s) represented by the chemicals tested**
Glyphosate herbicide	Glyphosate	Glyphosate
Neonicotinoid insecticides	Acetemiprid Clothianidin Dinotefuron Imidacloprid Thiacloprid Thiamethoxam	Acetemiprid Clothianidin Dinotefuron Imidacloprid Thiacloprid Thiamethoxam
Organophosphate insecticides	DMP (Dimethylphosphate) DMTP (Dimethylthiophosphate) DMDTP (Dimethyldithiophosphate)	Azinphos-methyl, chlorpyrifos-methyl, dichlorvos, dicrotophos, dimethoate, fenitrothion, fenthion, isazofos-methyl, malathion, methidathion, methyl parathion, naled, oxydemeton-methyl, phosmet, pirimiphos-methyl, temephos, tetrachlorvinphos, trichlorfon
	DEP (Diethylphosphate) DETP (Diethylthiophosphate) DEDTP (Diethyldithiophosphate)	Chlorethoxyphos, chlorpyrifos, coumaphos, diazinon, disulfoton, ethion, parathion, phorate, sulfotepp, terbufos

Lab methodology

Glyphosate

Health Research Institute has developed and validated a highly-sensitive test method for glyphosate and aminomethylphosphonic acid (AMPA) in foods, beverages, bodily fluids, soil, nutritional supplements, pharmaceuticals and environmental samples.

To address this and other challenges, we have adopted elements of the methods cited below and incorporated new elements for both sample extraction and LC-MS/MS analysis.

Sample extraction employed both physical and chemical extraction and fractionation steps to maximize recovery of glyphosate and aminomethylphosphonic acid, remove interfering substances and, in some cases, concentrate the analytes.

Each extract was analyzed by high-pressure liquid chromatography (LC) and linked to triple quadrupole mass spectroscopy (MS/MS), a system capable of specifically detecting and identifying different molecules and precisely measuring the amount of each molecule in the sample. This methodology is typically called “high-pressure liquid chromatography-triple quadrupole mass spectroscopy” or “LC-MS/MS” for short. The LC-MS/MS method developed by HRI simultaneously employs the standard addition method and the isotope dilution method, using analyte-specific internal standards for both glyphosate and AMPA. This method is accredited by the International Organization for Standardization to the ISO/IEC 17025 standard, which is used in assessing the competence of testing and calibration laboratories. In addition to ISO/IEC 17025 accreditation, the laboratory is also certified by the U.S. Center for Disease Control and Prevention’s CLIA program (Clinical Laboratory Improvement Amendments). Method-specific accuracy, precision, limit of quantitation and limit of detection for several different matrices are summarized below.

Glyphosate and AMPA

	Precision	Accuracy	LOQ	LOD
	%	%	ng/ml	ng/ml
Glyphosate	3.1	105	0.050	0.007
AMPA	3.3	95	0.050	0.006
Acceptance Criteria	<15%	70-120%		

Relevant references

Jensen, Pamela K., Chad E. Wujcik, Michelle K. McGuire, and Mark A. McGuire. 2016. Validation of Reliable and Selective Methods for Direct Determination of Glyphosate and Aminomethylphosphonic Acid in Milk and Urine Using LC-MS/MS. *Journal of Environmental Science and Health*. Part B 51 (4): 254–59. doi:10.1080/03601234.2015.1120619.

Chamkasem, Narong, Cynthia Morris, and Tiffany Harmon. 2016. Direct Determination of Glyphosate, Glufosinate, and AMPA in Milk by Liquid Chromatography/tandem Mass Spectrometry. *Journal of Regulatory Science*. 3 (2): 20–26.

Neonicotinoids and organophosphates

Sample extraction employed both physical and chemical extraction and fractionation steps to maximize recovery in food matrices such as whole apples, applesauce and spinach. Each extract was analyzed by high-pressure liquid chromatography (LC), coupled with triple quadrupole mass spectrometry (MS/MS). This is a system capable of specifically detecting and

identifying a wide range of compounds and precisely measuring the amount of each molecular species present in the sample. This methodology is typically called “high-pressure liquid chromatography-triple quadrupole mass spectroscopy” or “LC-MS/MS” for short. The LC-MS/MS method employed the isotope dilution method, using analyte-specific internal standards for all six neonicotinoids and six organophosphate metabolites. Method-specific accuracy, precision, limit of quantitation and limit of detection for several different matrices are summarized below.

Neonicotinoids

Analyte	Precision (std dev) at 1ng/mL	Accuracy (recovery) at 1ng/mL	LOQ	LOD
	%	%	ng/mL	ng/mL
Imidacloprid	8.91	98.66	1	0.329
Acetamiprid	6.1	99.89	1	0.228
Clothianidin	7.9	107.58	1	0.317
Dinotefuran	3.31	93.46	1	0.115
Thiacloprid	4.1	99.84	1	0.153
Thiamethoxam	9.87	105.31	1	0.388
Acceptance criteria	<15%	70-120%		

Organophosphates

Analyte	Precision (std dev) at 1ng/mL	Accuracy (recovery) at 1ng/mL	LOQ	LOD
	%	%	ng/mL	ng/mL
DMP	12.2	103.9	1	0.474
DMTP	5.65	104.3	1	0.374
DMDTP	4.2	104.6	1	0.164
DEP	10.9	95.11	1	0.388
DETP	5.75	99	1	0.213
DEDTP	6.75	106.57	1	0.269
Acceptance criteria	<15%	70-120%		

Relevant references:

Galeano, Michele Proietto et al. 2013. UHPLC/MS-MS Analysis of Six Neonicotinoids in Honey by Modified QuEChERS: Method Development, Validation, and Uncertainty Measurement. *International Journal of Food Science*. article id: 863904.

Odetokun, Martins, et al. 2010. Quantification of dialkylphosphate metabolites of organophosphorus insecticides in human urine using 96-well plate sample preparation and high-performance liquid chromatography–electrospray ionization-tandem mass spectrometry. *Journal of Chromatography B*. 878 (2010) 2567–2574.

Sinha, Sukesh Narayan et al. 2014. Analysis of dialkyl urine metabolites of organophosphate pesticides by a liquid chromatography mass spectrometry technique. *Analytical Methods, Royal Society of Chemistry.*

Snyder, Lloyd, Joseph J. Kirkland, John W. Dolan. 2010. *Introduction to Modern Liquid Chromatography, Third Edition*. John Wiley & Sons, Inc. Hoboken, NJ.