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Analysis of Glyphosate Residues in Foods from the Canadian Retail Markets between 2015 and 2017

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ABSTRACT: Underlying the risk management of pesticides to protect human health and to facilitate trade among nations are sound scientific data on the levels of compliance with standards set by governments and internationally from monitoring of the levels of pesticides in foods. Although glyphosate is among the universally used pesticides in the world, monitoring has been hampered by the analytical difficulties in dealing with this highly polar compound. Starting in 2015, using liquid chromatography/tandem mass spectrometry (LC-MS/MS) that permits accurate and reproducible determination of glyphosate, the prevalence, concentrations, and compliance rates were determined. In this work, the glyphosate residues contents of 7955 samples of fresh fruits and vegetables, milled grain products, pulse products, and finished foods collected from April 2015 to March 2017 in the Canadian retail market are reported. A total of 3366 samples (42.3%) contained detectable glyphosate residues. The compliance rate with Canadian regulations was 99.4%. There were 46 noncompliant samples. Health Canada determined that there was no long-term health risk to Canadian consumers from exposure to the levels of glyphosate found in the samples of a variety of foods surveyed. The high level of compliance (99.4% of samples with the Canadian regulatory limits) and the lack of a health risk for noncompliant samples indicate that, with respect to glyphosates, the food available for sale in Canada is safe.

KEYWORDS: *glyphosate residues, fruits, vegetables, grain products, pulse products, finished foods, Canada*

INTRODUCTION

Pesticides are an important tool used in food production, prolonging the shelf life and enhancing the trade of high-quality food, but their use must be balanced against risks of potential negative effects on human health from chronic exposure to these chemicals. The most widely used chemical herbicide is *N*-(phosphonomethyl) glycine, commonly referred to as glyphosate. Glyphosate (see Figure 1), marketed as

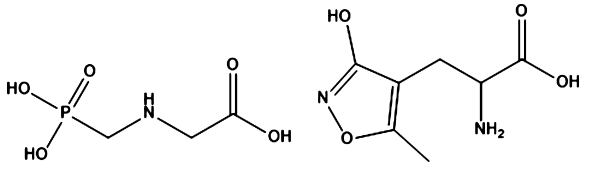

Figure 1. Chemical structures of glyphosate and its principal metabolite, aminomethylphosphonic acid (AMPA).

Roundup or Vision since 1974, is a broad spectrum herbicide used in agriculture and forestry.[5] Its agricultural uses include weed control before and after planting and desiccation of crops such as rice,[6] wheat,[7] and bean[8] to facilitate harvesting. Weeds can impede crop growth by competing for water, light, nutrients, and space; interfering with crop harvest; interfering with pollination; and harboring insects, diseases, or other pests.[9] Particular jurisdictions may permit some, all, or none of these uses; regulations and use patterns may change as new information becomes available.

The widespread and long-term use of glyphosate arises from its near-ideal characteristics as a broad spectrum herbicide. To take advantage of glyphosate's nonselective herbicide action, glyphosate-resistant transgenic crops (especially soybean,[10] cotton,[10] canola,[10] and corn[11]) have been produced and successfully used for a number of years. The advantages of glyphosate include its ease of use, its favorable economics of production,[11] and its low weed resistance.[12] Glyphosate is readily taken up through plant surfaces, but leaf uptake varies by species.[13] It is not an environmental issue because it does not leach into the water supply,[14] it binds strongly to soil,[15] it is less bioavailable than other herbicides, it is not persistent, it does not bioaccumulate because it is degraded by bacteria and fungi in the soil,[16] and it is nonvolatile.[17] Despite the advantages of glyphosate, the residue levels of glyphosate and the risk to consumers depend on the application technique, the environmental conditions, the stage of growth of plants, the volume of use, the water quality, and the use of coadjuvants.[5]

The human health effects have been evaluated by Health Canada (HC), the European Food Safety Authority (EFSA),[20] the U.S. Environmental Protection Agency (EPA),[21] and the

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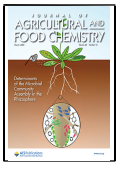

Joint Meeting of the Food and Agriculture Organization of the United Nations Committee (FAO) Panel of Experts on Pesticide Residues in Food and the Environment and the World Health Organization (WHO) Core Assessment Group on Pesticide Residues (JMPR).[22] Glyphosate is safe because neither glyphosate nor its primary degradation product, aminomethylphosphonic acid (AMPA), is associated with any known human health effects. Among other factors, human exposure through the diet is low because of low residue levels in foods,[18] and glyphosate disrupts an enzymatic pathway that exists in plants and fungi but not in animals or humans.[19] AMPA has a low toxicity to rats and has the same toxicological profile as glyphosate.[23] It should be noted, however, that there is controversy in the scientific community on the carcinogenicity of glyphosate. The International Agency for Research in Cancer (IARC) reclassified glyphosate as *probably carcinogenic to humans (Group 2A)* in 2015[24] due to a reanalysis of scientific studies in the literature.[24] In contrast, EFSA has concluded that glyphosate is "unlikely to pose a carcinogenic hazard to humans and the evidence does not support classification with regard to its carcinogenic potential".[25] This is supported by an American meta-analysis that failed to show an association between glyphosate exposure and the risk of development of lymphohematopoietic cancers.[26] In addition, a previous review had shown that the glyphosate was not genotoxic under normal conditions of exposure,[27] and a review of 7 cohort studies and 14 case-control studies in the United States showed no association between exposure to glyphosate and total cancer and/or site-specific cancer rates in adults or children.[28]

Other health effects of glyphosate depend on the amount ingested. Drinking 5 or 25 mL of glyphosate formulation generally resulted in only temporary gastrointestinal distress, whereas large amounts (85−200 mL of glyphosate formulation directly) can result in damage to the heart, kidney, and liver, difficulty breathing, loss of consciousness, or shock.[29] In addition, a study showed that glyphosate-based formulations have endocrine-disrupting effects on human liver cell lines at 0.5, 2, and 10 ppm levels.[30] Effects were seen in these human cell lines at all three levels, whereas regulatory levels of up to 20 ppm in foods[4] are permitted. Studies of glyphosate itself seem to indicate that it does not cause miscarriages, birth defects, or fertility effects,[37] but the case is not so clear for the formulations actually in use in the field. In particular, surfactant adjuvants such as polyoxyethylene tallow amines (POEAs, CAS 61791-26-2) are more toxic than the herbicide itself, causing adverse health effects on the heart, lungs, brain, and kidneys.[31,32] The French Agency for Food, Environmental and Occupational Health & Safety (ANSES)[33] and the European Commission[34] banned POEAs in herbicide formulations in 2016.

In Canada, the responsibility for ensuring the safety of the food supply to protect human health and permit fair trade practices is shared between two government partners, Health Canada and the Canadian Food Inspection Agency (CFIA). Health Canada sets the regulations while the CFIA enforces the regulations.[1] The Pest Management Regulatory Agency (PMRA) of Health Canada regulates the use of pesticides in Canada under the Pest Control Products Act[2] and performs the risk assessment for noncompliant samples. The PMRA establishes maximum residue limits (MRLs) for pesticide residues in food. The MRL is the maximum amount of residue that is expected to remain in or on food products when a pesticide is used according to label instructions. Pesticide MRLs apply to the identified raw agricultural commodity as well as to any processed food product that contains the commodity. Canadian MRLs apply to all foods available to Canadian consumers, whether the foods are domestically produced/grown or imported. The CFIA routinely monitors the compliance of pesticide residues in foods against Canadian standards by picking up samples at the manufacturer/distributor/retailer or importer level, testing for glyphosate residues, and assessing compliance against Canadian MRLs. Compliance is assessed against either specific MRLs[4] or the general MRL (GMRL) of 0.1 ppm, as stated in section B.15.002(1) of the Food and Drugs Regulations.[3]

Unfortunately, glyphosate and its metabolite, AMPA, were not monitored in foods by the CFIA prior to 2015. In 2015, Canadian lab capability to measure glyphosate residues was developed in a range of food matrices. Once the testing capability was available, the CFIA included this testing as part of its monitoring programs to assess product compliance. The MRLs for glyphosate in foods are presented in Table S1.

The aim of this study was to determine for the first time in Canada the prevalence and concentrations of glyphosate residues of the herbicide glyphosate in domestically produced and imported, organic and conventionally grown samples of raw agricultural commodities, processed fruits and vegetables, milled grains, pulses, and finished foods taken from the Canadian retail market under various monitoring programs in the period between 2015 and 2017. There is limited information available as to the source of glyphosate in food samples picked up at retail. It is not possible to directly correlate observed glyphosate levels with use patterns of glyphosate at the farm level.

MATERIALS AND METHODS

Sampling. A total of 7955 samples of domestic (n = 2122) and imported foods (n = 3622) as well as those of unknown origin (n = 2211 samples; insufficient information on the label to determine country of origin) were collected and analyzed for a range of residues and analytes, including glyphosate and AMPA, between 2015 and 2017. Food samples included a wide variety of fresh and processed fruit and vegetable products, grains (e.g., wheat, corn, oats, barley, buckwheat, and quinoa), beverages, pulses (bean, pea, lentil, chickpea), soy products, infant foods, and ready-to-eat/frozen meals. These foods were selected as being likely candidates to be exposed to glyphosate based on a review of available scientific literature, and the number of samples per food type was decided based on the relative importance in the diet (for FFV and PFV) or the market availability of a given ingredient in foods on the market, that is, how many different foods and brands have this raw commodity. Wheat can take the form of flour, bran, germ, grains, and a multitude of finished products, whereas oat is available in only a few forms (grains, bran, flour, cookies). Samples of fresh and processed fruits and vegetables were collected by CFIA inspection staff at importer warehouses and distribution centers in four regions (Atlantic Canada, Quebec, Ontario, and Western Canada), taking into account the collecting site and the country of origin. All samples of infant foods were purchased in a wide variety of retail stores in the Ottawa-Gatineau region of Canada. All other samples were purchased at retail locations (national chains, independent grocers, health food stores, pharmacies, ethnic stores) in six Canadian cities that encompass the four regions previously mentioned. Regardless of the food type, at least 250 g of a single lot was collected, wrapped in aluminum foil to protect from degradation by light, and shipped to testing laboratories, while maintaining sample integrity; that is, frozen samples remain frozen. Samples were homogenized, if necessary, and the glyphosate residue was extracted from a predefined amount of matrix. After

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Table 1. Prevalence and Levels of Glyphosate as a Function of Food Category

food type	MRL	foods	number of samples	number of samples with residues detected		range (ppm)[a]
				compliant[a]	noncompliant	
		Foods with a Single Ingredient or Class of Ingredient				
dairy and/or meat	0.08	plain yogurt, plain custard, milk-based infant formula, meat purees	22	0	0	n/a
fresh or processed fruits and vegetables (other than pulses, soybeans, and corn)	0.1	fresh/frozen/canned/pickled/dried fruits and/or vegetables, jams, juices/smoothies/nectars, fruit drinks, wine	1473	170	6	0.0002−0.15
other grains	0.1	whole grains and flour/starch of amaranth, arrowroot, buckwheat, rice, rye, triticale	626	156	35	0.005−5.9
corn and corn products	3	fresh/frozen corn, gluten-free baking mixes/cookies/crackers/pasta, popcorn, corn flour, cornmeal, corn chips, corn bran, corn starch, tacos/tortillas	501	115	0	0.0006−0.45
beans and/or chickpeas and/or lentils and/or peas	4 or 5	fresh/frozen/canned/dried/baked/refried/beans/chickpeas/lentils/peas, chickpea/lentil/pea chips, flours	770	327	5	0.003−13
wheat and wheat products	5 or 15	wheat bran, baking mixes, couscous, wheat flour, wheat germ, bulgur, wheatlets, pasta (except for gluten-free), plain cookies and crackers	807	616	0	0.005−8.5
barley and barley products	10	pot/pearl barley, barley flakes, barley flour	103	51	0	0.0058−2.1
oats and Oat Products	15 or 35	baking mixes, oats, oat bran, oat flour, oatmeal	310	231	0	0.006−3.1
soy and soy products	20	fresh/dried/frozen soybeans/edamame, soy beverages, soy flour, meat alternatives, soy nuts, tofu, soy desserts, miso	204	20	0	0.0051−6.0
		Foods with Multiple Ingredients or Classes of Ingredients				
infant foods	0.1−35 ppm	infant cereals, toddler snacks, granola bars/cereal bars, infant/toddler meals, purees, infant formula, teething biscuits, fruit-flavored yogurt/fresh cheese	927	290	0	0.006−2.5
manufactured foods intended for general population	0.1−35 ppm	cookies, crackers, frozen meals, canned pasta, frozen pizza, soup, gluten-free pasta	2212	1344	0	0.0001−1.9

[a]Compliant refers to detectable levels of glyphosate that are at or below the applicable MRL (i.e., compliant with Canadian regulations).

homogenization and/or extraction, all samples were stored in a −80 °C freezer until analysis and for at least 90 days to permit retesting if needed. All samples were analyzed prior to their best-before date; however, the shelf life and best-before date were not considered when selecting products.

Sample Preparation, Standard Preparation, and Analysis. Samples were analyzed in two ISO/IEC 17025 accredited laboratories. The methods have been demonstrated to provide accurate results via internationally accredited proficiency testing (PT) programs as well as interlaboratory sample comparison. The laboratories are also required to provide the CFIA with the results of their PT programs as well as any corrective actions needed associated with poor performance in these programs. Additionally, when the laboratories identify residue levels within 80% of the MRL for a particular commodity, they are required to repeat the assay to verify the results.

Method 1.[35] The sample was extracted in 0.05 M KOH in the presence of isotopically labeled internal standard. After centrifugation, the extract was adjusted to pH 7.0 ± 0.5 with 0.1 M HCl. Following the addition of 5% sodium thiosulfate and sodium tetraborate, the sample extract was derivatized with fluorenylmethyloxycarbonyl chloride (FMOC-Cl). The reaction quenched, filtered, and analyzed by HPLC-MS/MS.[38]

Method 2.[36] The sample was extracted in water in the presence of isotopically labeled internal standard. After centrifugation, the extract was acidified with 2% phosphoric acid and passed through a polystyrene−divinylbenzene solid-phase extraction cartridge. The final extract was analyzed by HPLC-MS/MS.[39]

With both methods, the samples were analyzed using reverse-phase liquid chromatography with gradient elution. Detection was performed by tandem mass spectrometry with electrospray ionization in negative mode. Two of the marker residues were analyzed (glyphosate and its metabolite, AMPA), and two transitions were monitored for each analyte. For glyphosate, method 1 monitored m/z 390.0 to m/z 150.0 and m/z 390.0 to m/z 168.0, and method 2 measured m/z 167.8 to m/z 149.9 and m/z 167.8 to m/z 62.8. For AMPA, method 1 monitored m/z 110.0 to m/z 63.0 and m/z 110.0 to m/z 79.0, whereas method 2 recorded m/z 109.9 to m/z 81.0 and m/z 109.9 to m/z 62.8.

All results were assessed using the Canadian MRLs, which are listed in Table S1.

Quality Assurance/Quality Control (QA/QC) of Data and Reporting. The glyphosate concentration reported, as measured by the analytical method, was the final concentration in the sample and was the sum of glyphosate and AMPA levels. When residue levels are within 80% of the MRL for a particular commodity, it is required that the assay be repeated to verify the results. In addition, the data are scrutinized to ensure the accuracy of the sampling information. In the case of a single-ingredient food, such as wheat flour, product compliance was determined by a comparison of the reported level of glyphosate residues (sum of Gly + AMPA) to the MRLs published in Health Canada's Pesticide MRL database.[4] In the case of multi-ingredient foods, the assessment of detected residues was performed by examining the MRL of each ingredient listed in the ingredient list. (An ingredient may be made from another food. Where possible, the MRL for the product as listed is used; otherwise, the source of the food is used. For example, wine may be used as a flavoring ingredient. If there is an MRL available for wine, then that MRL will be used in the assessment; if there is no MRL for wine, then the MRL for grapes will be used.) The highest MRL available, regardless of where it was listed in the ingredient list, was used for the final assessment of whether a sample was compliant. Many food−pesticide combinations do not have specific MRLs; in Canada, there is a default MRL (0.1 ppm) that was used for assessments.

All data are assessed against the applicable MRLs. All concentrations below the limit of detection (LOD) of the method are reported as zeros and are deemed "nondetectable". Samples with glyphosate concentrations between the LOD and the MRL (inclusive) are referred to as "compliant" residues. Samples with glyphosate levels above the MRL are deemed "noncompliant". Prevalence represents the percentage of samples with detectable levels of glyphosate, whether compliant or noncompliant.

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Statistical Analysis. The target sample population consisted of all units of the targeted commodities available at retail to Canadian consumers as per the sampling design. Because all units of the population could not be assumed to have an equal probability of selection, the commodity units at a store were drawn by the sampler as randomly as possible to be reasonably representative of the population. The sampling method used for the monitoring programs is a nonprobability sampling method, which does not allow standard statistical inferential methods to be invoked. Nevertheless, the random selection approach and the choice of multiple cities provide a snapshot of the presence of glyphosate in the selected foods.

RESULTS AND DISCUSSION

The Supporting Information presents the Canadian and international maximum levels adopted for glyphosate (Table S1) and a further breakdown of the glyphosate results from the commodity level to specific product types (Tables S2−S7). In Canada, it is the role of HC to determine if residue levels pose a risk to consumers. They have reviewed the data and have determined that the levels in all products tested did not pose a risk to consumers. MRLs are set at levels well below a level that would pose a risk to consumers; simply exceeding an MRL does not subsequently mean that the products pose a risk to consumers' health.

Overview. The CFIA analyzed 7955 samples of foods to determine the level of compliance of foods in the Canadian marketplace against established MRLs. Testing results are grouped by food categories (Table 1). Of the samples tested, 3366 samples (42.3%) contained detectable glyphosate residues, and only 46 samples (0.6%) were determined to be noncompliant with applicable Canadian regulations. The noncompliant samples included 15 samples of buckwheat flour/groats (0.11 to 2.1 ppm), 7 samples of whole millet (0.22 to 1.5 ppm), 7 samples of rye flour (0.20 and 5.9 ppm), 4 samples of millet flour (0.11 to 0.46 ppm), 3 samples of chickpea flours (4.2 to 13 ppm), 2 samples of grapefruit juice (0.11 and 0.15 ppm), 2 samples of mixed grains (0.19 and 0.52 ppm), 2 samples of beans (8.4 and 8.6 ppm), 2 samples of fresh mushrooms (0.11 and 0.21 ppm), 1 sample of fresh apples (0.20 ppm), and 1 sample of fresh limes (0.12 ppm). Of these food types, only beans and chickpeas are subject to a 4 ppm MRL; the remaining products are subject to the 0.1 ppm GMRL. The 46 noncompliant samples include 15 organic products and 31 conventionally grown products. All samples of foods for infants (e.g., snacks, meals, juices, and cereals) were compliant with applicable glyphosate MRLs. Health Canada determined that there was no health risk to consumers, including infants and toddlers, through the consumption of foods with the levels of glyphosate observed in these studies[40] The observed compliance rates (overall and for infant foods) are comparable to the levels of compliance observed for other pesticides tested under CFIA programs. The high compliance rate also confirms that the food available for sale in Canada is safe for consumers.

Although the compliance is high, it is important to examine the data (compliant and noncompliant) for any trends to determine what actions are necessary on the Agency's part. The data were examined as a function of country of origin and type of food and are presented as follows.

Country of Origin as Related to Compliance. Despite the high compliance, the data were analyzed to determine whether there were any trends with respect to country of origin. Of the samples taken, 2122 samples were of domestic origin, 3622 samples were of imported origin (from at least 66 countries), and 2211 samples were of unknown origin (insufficient information on the label to determine the country of origin). The compliance rates for foods of domestic, imported, and unknown origins were 99.5, 99.3, and 99.4%, respectively. The number of noncompliances was 9 (4 rye flours, 2 chickpea samples, 2 mushroom samples, and 1 apple sample) for Canada, 12 (3 millet grains, 3 rye flours, 2 grapefruit juices, 2 mixed grains, 1 buckwheat flour, and 1 kidney bean) for the unknown country of origin, and 25 for imported products. The noncompliances were associated with four countries for imported products: the United States (21 in all, consisting of 12 buckwheat flours, 4 millet flours, 3 millet grains, 1 bean flour, and 1 chickpea flour), Poland (2 samples of buckwheat groats), Mexico (1 lime), and the Russian Federation (1 millet). The difference in compliance among the different countries may be related to the types of foods imported and the volume of imports. The reason why there are more noncompliances associated with food products from the U.S. is because Canada imports more agricultural food products from the U.S. than from other countries. Another consideration may be that the exporting countries permit higher maximum levels in their foods; however, once the food is exported to Canada, it is subject to the Canadian regulations.

Effects of Processing on Final Glyphosate Levels. Glyphosate levels may be affected by the food processing steps. Washing, heating, the removal of the hull/husk/shell, and treatment with strong acids/bases may cause a loss of glyphosate, whereas drying may increase the concentration of glyphosate in the finished product relative to the raw agricultural commodity. In cases where multiple ingredients may have been treated with glyphosate, the final glyphosate levels will depend on the both the relative levels of contamination in each ingredient and their relative contribution to the final mass of the finished food.

Food Type as Related to Compliance. The prevalence and levels of glyphosate as a function of types of foods are presented in Table 1. The food categories have been subdivided based on whether the food consists of a single ingredient/class of ingredients (e.g., most fruits and vegetables are subject to the 0.1 ppm standard), where all ingredients are subject to a single MRL, or consists of multiple ingredients/classes of ingredients, where all ingredients are subject to two or more MRLs. All foods were analyzed as sold; that is, samples were not washed, cooked, or used as ingredients. These measures may cause a decrease in the glyphosate level; therefore, the levels detected in this survey would represent the highest concentrations to which a consumer could potentially be exposed.

The prevalence of glyphosate was low (0−15%) in dairy- and/or meat-based foods, fresh fruits and vegetables, and soy products; medium (20−45%) in other grain products (e.g., buckwheat, quinoa), corn and corn products, and pulses; and high (50−76%) in wheat products, barley products, and oat products. This order is not conserved when looking at the maximum observed glyphosate level. The highest glyphosate levels were observed in pulses and wheat products (where glyphosate was approved as a harvesting aid in some jurisdictions during the period of this study), whereas the lowest were observed in fresh fruits and vegetables (glyphosate may or may not be applied directly to crops) and corn products (husk would contain most of the glyphosate; it is removed before any products are made).

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Table 2. Glyphosate Results for Fresh and Processed Fruits and/or Vegetables

food type	number of samples	number of samples with residues detected		MRL (ppm)	range (ppm)[a]
		compliant	noncompliant		
Fresh Fruits and Vegetables					
fruit	307	37	2	0.1	0.0013−0.20
herbs and spices	19	3	0	0.1	0.0021−0.05
mushrooms	11	7	2	0.1	0.0052−0.21
vegetables	327	14	0	0.1	0.001−0.023
Processed Fruits and Vegetables, Beverages, and Jams					
canned foods	132	10	0	0.1	0.0008−0.023
dried foods	1	0		0.1	n/a
frozen foods	70	7	0	0.1	0.0016−0.062
jams	6	1	0	0.1	0.017
juice concentrates	42	9	0	0.1	0.0042−0.038
pickled vegetables	13	4	0	0.1	0.001−0.013
miscellaneous processed fruits and/or vegetables	17	16	0	0.1	
beverages	499	79	2	0.1	0.002−0.15
vegetarian meals for general population	29	0	0	0.1	n/a

[a]Range (ppm) includes only samples with residues detected.

Among the multiple ingredient foods, 31% of infant foods and 61% of foods intended for the general population contained detectable levels of glyphosate. This may be related to the types of foods, the type and degree of processing, and/or the manufacturers of infant foods being pro-active in using ingredients with low or no pesticide levels. The highest observed glyphosate concentrations in single foods ranged from 0.15 ppm in dairy- and/or meat-based foods to 13 ppm in pulses. The highest observed glyphosate levels were 2.5 ppm in infant foods and 1.9 ppm in foods for the general population.

Dairy/Meat. This was the smallest category, with a total of 22 samples. This included a total of 10 dairy-based products and 12 meat-based products. (See Table S2 for more information on the samples tested.) Glyphosate was not detected in any sample. As expected, whatever the source of the glyphosate, glyphosate was not detected in these products because the animal will metabolize and eliminate the pesticide before it can transfer to the milk or meat.

Fresh or Processed Fruits and Vegetables (Other than Pulses, Soybeans, and Corn). This was one of the larger categories. All products must comply with the GMRL. The study encompassed 1473 samples, including 83 types of fresh fruits and vegetables, 118 types of fruit- and/or vegetable-based processed products, and 19 types of juices/fruit beverages/nectars. Glyphosate was not detected in 1297 samples (88%) of the samples; 170 contained measurable but compliant residues, and 6 were noncompliant. The noncompliances were observed in two samples of fresh mushrooms, two samples of grapefruit juice, one sample of fresh apples, and one sample of fresh limes. Five of the six noncompliant samples were for domestically grown products; the lime sample was imported. The overall compliance rate for this category was 99.6%. For more information on the prevalence and levels of glyphosate per individual food, see Table S3 for fresh fruits and vegetables and Table S4 for processed fruits and vegetables, beverages, and jams. Note that juice concentrates, as described in this section, are used by juice manufacturers to produce ready-to-drink beverages. All other beverages were ready-to-drink.

Table 2 shows a breakdown of the glyphosate prevalence and levels as a function of food type. The prevalence of glyphosate was high only in mushrooms; the remaining foods were associated with a low or medium prevalence. The levels of glyphosate were quite low in this food category. Excluding the four noncompliant results, the highest observed glyphosate levels in fresh fruits and vegetables and in fruit- and/or vegetable-based processed products were 0.085 and 0.062 ppm, respectively.

Comparing glyphosate prevalence and levels in fresh fruits and vegetables with their corresponding processed products, even with samples taken from unrelated shipments, most of the commodities were consistent in that glyphosate was not detected in either the fresh or the processed form. Some commodities, such as apples, mangos, grapefruits, lemons, plums, potatoes, and sweet potatoes, had detectable glyphosate residues in the fresh form but not in processed form. On the contrary, oranges, grapes, blueberries, cherries, mushrooms, tomatoes, and asparagus all demonstrated some detectable but compliant residue results for both fresh and processed products.

Other Grains. This category, consisting of nine nonstaple grains, included milled grains and flours, all subject to the 0.1 ppm GMRL. The study encompassed 631 samples in this category. Of the samples analyzed, 156 contained measurable but compliant residues, and 35 were found to be noncompliant. Only four grains were associated with noncompliances: buckwheat (n = 15), millet (n = 11), rye (n = 7), and mixed grains (n = 2). All of the noncompliances in this category were associated with imported products. The compliance rate for this category was 94.4%; this represents the lowest compliance rate of the survey. For more information on the prevalence and levels of glyphosate per individual food, please see Table S5.

The glyphosate prevalence was analyzed as a function of grain type. Glyphosate was not detected in arrowroot samples. The remaining eight grains had detection rates ranging from 7 to 54%; the percentage of compliant residue levels declined in the order: millet > rye > buckwheat ≫ rice > mixed grains > teff > quinoa > amaranth. The maximum observed concentration of glyphosate declined in the order: rye > buckwheat > millet > mixed grains > amaranth > teff > rice > quinoa. The observed prevalence and concentrations of

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Table 3. Prevalence and Concentrations of Glyphosate in Corn and Corn Products

food	form	number of samples			MRL (ppm)	range (ppm)[a]
		total	compliant residues levels	noncompliant		
corn and corn products	fresh corn	4	0	0	3	n/a
	canned corn	8	0	0	3	n/a
	frozen corn	4	1	0	3	0.067
	corn chips	91	28	0	3	0.0051−0.045
	corn flour	97	39	0	3	0.0052−0.30
	cornmeal	103	30	0	3	0.0052−0.32
	tacos/corn pasta/toasted corn	94	11	0	3	0.005−0.098
	corn starch	50	3	0	3	0.0086−0.45
	popcorn	49	3	0	3	0.018−0.020
	couscous (corn)	1	1	0	3	0.092

[a]Range (ppm) includes only positive results.

Table 4. Prevalence and Concentrations of Glyphosate in Pulses and Pulse Products

food	form	number of samples			MRL (ppm)	range (ppm)[a]
		total	compliant residues	noncompliant		
beans	fresh	11	0	0	4	n/a
	frozen	4	0	0	4	n/a
	canned	199	72	0	4	0.0054−0.43
	dried	126	52	1	4	0.0051- 8.6
	flour	43	27	1	4	0.01−8.4
	products	4	1	0	4	0.0059
chickpeas	canned	30	15	0	4	0.16−2.8
	dried	20	9	0	4	0.006−2.4
	flour	57	12	3	4	0.016−13
	products	30	17	0	4	0.00079−3.2
lentils	canned	16	7	0	4	0.0028−0.4
	dried	42	21	0	4	0.021−2.6
	flour	49	8	0	4	0.0059−0.2
	products	12	3	0	4	0.0093−0.06
peas	fresh	4	0	0	5	n/a
	canned	37	5	0	5	0.003−0.052
	frozen	5	1	0	5	0.0055
	dried	35	25	0	5	0.0051−0.81
	flour	38	23	0	5	0.021−1.2
	products	3	1	0	5	0.074
mixed vegetables containing one or more pulses	canned	4	1	0	4	0.013
	frozen	1	0	0	4	n/a

[a]Range (ppm) includes only positive results.

glyphosate are likely to be related to the use patterns of glyphosate in growing these crops (from preplanting to preharvest) and the ability of the plant to absorb glyphosate.

Health Canada determined that there was no health risk to consumers, including heavy consumers of these products because of the high overall compliance rate. All violations involved the exceedance of the GMRL (0.1 ppm) and the existence of the MRLs for glyphosate in staple products that are much higher than those detected (e.g., 20 ppm for soy, 5 or 15 ppm for wheat, 3 ppm for corn, and 15 or 35 ppm for oats).

Corn and Corn Products. Corn is widely consumed by all age groups. This was one of the smaller categories, encompassing 501 samples; 115 samples contained compliant residue levels, and 0 samples were noncompliant. This category included fresh/canned/frozen corn, cornmeal, corn flour, corn starch, and foods that listed one of these products in their ingredient list (e.g., corn chips). The overall compliance rate for this MRL was 100%. Table 3 shows a breakdown of the glyphosate prevalence and levels as a function of food type. All of the corn-based samples were associated with a low (0−15%) or medium (16−45%) prevalence. The maximum observed concentration of glyphosate was 0.45 ppm, which is almost 10 times below the MRL of 3 ppm. The maximum observed concentration of glyphosate declined in the order: corn starch > cornmeal, corn flour > tacos/corn pasta/toasted corn > frozen corn > corn chips > popcorn.

The levels of glyphosate in finished food products were generally higher than those in the fresh corn. The processing steps may be increasing the concentration of glyphosate, or the finished food products were made from corn with higher glyphosate levels.

Pulses (Beans and/or Chickpeas and/or Lentils and/or Peas). Pulses are widely consumed by all age groups in Canada. This category encompassed 770 samples; 327 samples contained compliant residue levels, and 5 samples were noncompliant (2 for bean products and 3 for chickpea products). The noncompliant samples originated in Canada (2) and the U.S. (2), and the country of origin could not be

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Table 5. Prevalence and Concentrations of Glyphosate in Wheat and Wheat Products

food	form	number of samples			MRL (ppm)	range (ppm)[a]
		total	compliant residues	noncompliant		
wheat and wheat products	bran	100	95	0	15	0.013−8.5
	flour	230	178	0	5	0.0054−0.82
	cookies	11	9	0	5	0.0088−0.16
	couscous	66	50	0	5	0.0056−1.1
	crackers	10	9	0	5	0.011−0.38
	pasta	221	175	0	5	0.005−1.4
	bulgur wheat	43	27	0	5	0.005−0.21
	cream of wheat	15	13	0	5	0.006−0.51
	gluten/wheat berries/wheatlets	21	11	0	5	0.0066−0.94
	kamut	42	19	0	5	0.0055−0.06
	spelt	29	13	0	5	0.005−0.058
	wheat germ	19	17	0	5	0.016−0.9

[a]Range (ppm) includes only positive results.

Table 6. Prevalence and Concentrations of Glyphosate in Barley and Barley Products

food	form	number of samples			MRL (ppm)	range (ppm)[a]
		total	compliant residues	noncompliant		
barley and barley products	flour	52	25	0	10	0.0063−1.6
	pearl barley	32	18	0	10	0.0077−2.1
	pot barley	14	7	0	10	0.0058−0.15
	whole barley	5	1	0	10	0.098

[a]Range (ppm) includes only positive results.

determined for one sample. This category included fresh/frozen/canned/dried/baked/refried beans, chickpeas and lentils, flours made from these pulses, and chickpea/lentil/pea chips and flour. The overall compliance rate for this category was 99.3%. Table 4 shows a breakdown of the glyphosate prevalence and levels as a function of food type. The results indicated that the rates of residue detection in samples decreased in the following order: 41% for chickpeas, 40% for beans, 33% for lentils, and 22% for peas. The overall percentage for pulses was higher than that in any products in the preceding sections. The maximum observed concentrations decreased in the order: 13 ppm for chickpeas, 8.6 ppm in beans, 2.6 ppm in lentils, and 1.2 ppm in peas. Both the prevalence and concentrations of glyphosate in these products appear to be consistent with the possible use of glyphosate as a harvest aid, approved for use in Canada and other jurisdictions at the time of the study. For both peas and beans, glyphosate was not detected in the raw agricultural commodity but was detected to some extent in the finished products. A concentration effect of drying equivalent to the moisture level in the plants may need to be applied to these products. Separate MRLs may be available for dried and field products.

Wheat and Wheat Products. This category represents the most highly consumed staple grain in Canada. This category encompassed 807 samples; 616 contained compliant residue levels, and 0 samples were noncompliant. The overall compliance rate for this category was 100%. These foods were subject to one of two MRLs: 15 ppm for wheat bran and 5 ppm for couscous, wheat flour, wheat germ, bulgur, wheatlets, dry/fresh/frozen pasta (except for gluten-free), plain cookies, and plain crackers. Table 5 shows a breakdown of the glyphosate prevalence and levels as a function of food type.

The percentage of samples with detected residues per type of food decreased in the order: wheat bran (95%) > crackers (91%) > cream of wheat (87%) > cookies (82%) > pasta (79%) > flour (77%) > couscous (76%) > germ (63%) > gluten/wheat berries/wheatlets (48%) > kamut and spelt (45%) > bulgur (37%). The highest observed glyphosate level per food product type ranged from 0.06 ppm in kamut/spelt grains to 8.5 in wheat bran. This is consistent with the fact that the bran is on the outside of the plant and would have the greatest exposure to any glyphosate applied. Where products were made with whole wheat flour or incorporated bran, the levels of glyphosate were higher (data not shown). The percentage of samples with detected residues for wheat (alone or in combination) was much higher than that for any other product examined in previous sections. Despite this, the highest concentration of glyphosate was well below the MRL. For the other food products detailed in Table 5, the highest concentration observed was 3.5 to 83 times lower than the MRL. These results confirmed that glyphosate was being used appropriately in the field and does not represent a health risk to consumers.

Barley and Barley Products. This small category encompassed 103 samples; 51 samples contained compliant residue levels, and 0 samples were noncompliant. Table 6 shows a breakdown of the glyphosate prevalence and levels as a function of the type of barley-based product.

The percentage of samples with detected residues for all barley products (except whole barley) was ∼50%. This was somewhat lower than the percentage observed with wheat but higher than the results observed with pulses. The highest observed glyphosate concentrations were observed in pearl barley and barley flour. However, the overall compliance rate was 100%, and the observed highest concentrations were 2.3 to 51 times below the applicable MRL.

Oats and Oat Products. This category included 310 samples; 231 samples contained compliant residues levels, and 0 samples were noncompliant. The overall compliance rate for this category was 100%. These foods were subject to one of

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Table 7. Prevalence and Concentrations of Glyphosate in Oats and Oat Products

food	form	number of samples			MRL (ppm)	range (ppm)[a]
		total	compliant residues	noncompliant		
oats and oat products	oats	105	80	0	15	0.006−1.7
	oatmeal	56	48	0	15	0.011−1.4
	oat flour	100	66	0	15	0.0061−3.1
	oat bran	49	37	0	35	0.0071−2.1

[a]Range (ppm) includes only positive results.

Table 8. Prevalence and Concentrations of Glyphosate in Soybeans and Soy Products

food	form	number of samples			MRL (ppm)	range (ppm)[a]
		total	with compliant residues	noncompliant		
soy-based foods	canned soybeans	10	0	0	20	n/a
	dried soybeans	25	3	0	20	0.0069−0.024
	frozen soybeans	18	1	0	20	0.013
	beverage	51	1	0	20	0.0051
	flour	30	11	0	20	0.0052−6.0
	meat alternative	12	2	0	20	0.015−0.016
	soy products	10	2	0	20	0.013−0.05
	tofu	48	0	0	20	n/a

[a]Range (ppm) includes only positive results.

two MRLs: 35 ppm for oat bran and 15 ppm for oats, oatmeal, and oat flour. Table 7 shows a breakdown of the glyphosate prevalence and levels as a function of type of oat-based product. Most of the food products listed in Table 7 are consumed after cooking or are used as ingredients.

As seen in Table 7, the percentage of samples with detected residues for all oat products (except oat flour) was ∼75%. Similar to barley products, this was somewhat lower than the percentage observed with wheat but higher than the results observed with pulses. The highest observed glyphosate concentration was observed in oat flour. However, the overall compliance rate is 100%, and the observed highest concentrations were 4.8 to 17 times below the applicable MRLs.

Soy and Soy Products. The products included canned/frozen soybeans and soy-derived products like soy beverages and meat alternatives. This category encompassed 204 samples; 20 samples contained compliant residue levels, and 0 samples were noncompliant. The overall compliance rate for this category was 100%. Table 8 shows a breakdown of the glyphosate prevalence and levels as a function of the type of soy-based product

As seen in Table 8, the percentage of samples with residues ranged from 0 (canned soybeans and tofu) to 37% in soy flour. These were among the lowest rates of detectable glyphosate prevalence and glyphosate levels observed. The maximum observed glyphosate per product ranged from 0.013 (frozen soybeans) to 6.0 ppm (soy flour). This is consistent with surveys for other contaminants in soy products, where soy flour was typically associated with the higher level of contaminants among soy products. The overall compliance rate was 100%, and the observed highest concentrations were 3 to 1500 times below the applicable MRL.

Infant Foods. These products are marketed specifically to infants and small children, through product placement or pictures/cartoons on the label. In this survey, it included foods such as infant formula, infant cereals, fruit/vegetable purees, teething biscuits, infant/toddler snacks, and meals for infants and toddlers. These foods may be subject to two or more MRLs, depending on the ingredient list. The applicable MRLs ranged from 0.08 to 35 ppm.

This category encompassed 927 samples; 290 samples contained compliant levels of residues, and 0 samples were noncompliant. The overall compliance rate for this category was 100%. For more information on the prevalence and levels of glyphosate per individual food, see Table S6.

As a general rule, foods that contained grains and/or pulses were more likely to have detectable glyphosate levels (39 and 42%, respectively, versus 15% in fruit- and/or vegetable-based foods) and higher observed glyphosate concentrations (the maximum observed concentration was 2.5 ppm for grains, 0.088 ppm for pulses, and 0.11 ppm for fruit- and/or vegetable-based foods). This is consistent with the results and explanations noted in the single-ingredient discussions.

Manufactured Foods Intended for General Population. This category included any foods marketed to the general public that consisted of two or more ingredients that could contain glyphosate. The applied MRLs ranged from 0.08 to 35 ppm.

There were 2180 samples; 1344 samples contained compliant levels of residues, and 0 samples were noncompliant. The overall compliance rate for this category was 100%. For more information on the prevalence and levels of glyphosate per individual food, see Table S7.

As a general rule, foods in this category that contained grains and/or pulses were more likely to have detectable glyphosate levels and higher observed glyphosate concentrations. This is consistent with the results and explanations noted in the single-ingredient discussions.

All Foods in Survey. Examining the data as a whole indicates that most of the samples, regardless of their complexity, were compliant with Canadian regulations. (See Table 1 and the Supporting Information.) In addition, grains and pulses (beans, chickpeas, lentils, and peas) were associated with the highest levels of samples with detected but compliant residue levels, the highestnumber of noncompliances, and the

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Table 9. Comparison of Compliance Rate for Glyphosate for Grain-based Products in the Marketplace in Different Jurisdictions

	percentage compliance				
commodity	CFIA study	FSANZ35	EFSA	U.K.	U.S.
wheat	100	100	100	100	not reported
corn	100	100	100	100	100
oats	100	98.6	100	100	not reported
rice	100	not reported	100	100	not reported
barley	100	100	100	100	not reported
rye	91.1	not reported	100	not reported	not reported

Table 10. Comparison of Compliance Rate for Glyphosate for Pulse-based Products, Soy Products, and Pasta in the Marketplace in Different Jurisdictions

	percentage compliance				
commodity	CFIA study	FSANZ	EFSA	U.K.	U.S.
beans	99.5	100	100[a]	not reported	not reported
chickpeas	97.8	99.8	100[a]	not reported	not reported
lentils	100	100	86.4	not reported	not reported
peas	100	100	100	not reported	not reported
soy-based products	100	100	100	not reported	100
pasta	100	not reported	not reported	100	not reported

[a]There was one noncompliant sample in 2014, but the total number of bean/chickpea samples analyzed for glyphosate in 2014 was not reported. Thus the 2014 data were excluded.

highest maximum observed concentrations. This is consistent with the common modes of application of glyphosate in the field (preplanting, during growth, as harvest aid) and the plant physiology. A tough outer shell minimizes the absorption of glyphosate into the edible portion.

Organics. There were a total of 1504 products labeled as organic (on the product label or accompanying documentation) that were sampled over the 2 year period. These samples are subject to two levels of regulations: They are assessed against the applicable MRLs for glyphosate like all other foods, and they are also regulated under the Organic Product Regulations (OPR). Organic products, like their conventionally grown counterparts, may be compliant or noncompliant with the applicable MRLs. The OPR prohibits the direct use of synthetic pesticides like glyphosate at any point of the food chain (from preplanting to product available to consumers). Organic products may have detectable levels, as samples may be contaminated by drift from adjacent farms where pesticides are used, environmental contamination (e.g., pesticides remain in water or soil), or transfer from contaminated trucks, bins, or other devices used in product storage or transport. The detected level of glyphosate may point to the source of the contamination. Very low levels are likely the result of environmental contamination (<5% of the MRL), whereas levels that are close to or exceed established product-specific MRLs are more likely associated with deliberate use. This distinction is more clear-cut when dealing with product-specific MRLs than with exceeding the GMRL.

The analysis indicated that 75% of the samples of products labeled as organic did not contain detectable glyphosate residues (as compared with 51% for conventionally grown products). Fifteen samples contained glyphosate residue levels that exceeded the GMRL of 0.1 ppm (13 buckwheat and 2 millet), all of imported origin. Of the remaining 354 samples where glyphosate was detected, 220 samples (58%) contained glyphosate residue levels that were 5% or less than the applicable MRL. Investigation of the source of the pesticide residue is required to determine whether it is the result of deliberate use or accidental exposure of the commodity to glyphosate. The glyphosate residue levels in the remaining 134 samples ranged from 5.2 to 99.3% of the applicable MRLs for the given food commodity. These levels require investigation of the source of the pesticide, but accidental exposure is less likely at these levels.

Data Comparison to Other Jurisdictions. Residue monitoring data from other jurisdictions were compared to the results from our study where possible. The areas reviewed included Food Standards Australia New Zealand (FSANZ),[41] the EFSA,[42−48] the United Kingdom,[49] and the United States.[50] All available data on glyphosate testing were downloaded and combined (if there were multiple years of data) and are summarized in Table 9 for grains and Table 10 for pulses and other foods. Because there were different methodologies used for the analysis of the data (i.e., different LODs/LOQs) and different ways of reporting the data (e.g., from LOD to maximum concentration, 0.5 MRL to greater than MRL, LOQ to maximum concentration), only the compliance rates with regulations in the respective country/region were compared. It is acknowledged that there are differences in MRLs between jurisdictions, but they are generally comparable.

The results presented in Tables 9 and 10 show that the compliance rates for glyphosate are high for the crops studied, regardless of jurisdiction. For grain-based foods, only one crop (Canadian rye) had a compliance rate <100%. This may be accounted for by the difference in the applicable MRLs across jurisdictions (10 ppm for EFSA versus 0.1 ppm in Canada). The trend for pulse-based foods is less clear. Peas had 100% compliance regardless of jurisdiction, the compliance rates were lower for beans/chickpeas in Canada relative to the other jurisdictions, whereas the compliance rate for lentils was 100% in Canada and Australia/New Zealand but was lower for the EU. For the pulse-based foods, these differences may result from the types of samples tested (dried/frozen/canned pulse

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and pulse-derived products in Canada versus fresh/dried commodities for the other jurisdictions), the different use patterns for glyphosate in the field, and/or differences in the applicable MRL. All soy-based samples and pasta samples were 100% compliant regardless of jurisdiction. The high compliance rates and the comparability of results confirm that glyphosate is being used appropriately and similarly in all jurisdictions cited.

The compliance rate with Canadian regulations was 99.4%. There were 46 noncompliant samples. Health Canada determined that there was no long-term health risk to Canadian consumers from exposure to the levels of glyphosate found in the samples of a variety of foods surveyed. All foods targeted at infants, toddlers, and children were compliant and thus were unlikely to cause exposure to infants and young children. The CFIA will continue to monitor glyphosate levels in food products available in the Canadian retail space to fulfill its mandate of ensuring the safety of the Canadian food supply.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jafc.9b07819.

Table S1. MRLs of glyphosate (sum of concentrations of glyphosate + AMPA) in food. Table S2. Distribution of dairy/meat-only samples. Table S3 Distribution of fresh fruit and vegetable samples in terms of number of samples, number of compliant and noncompliant residues, and the ranges of glyphosate concentrations detected. Table S4. Distribution of processed fruit and vegetable samples in terms of number of samples, number of compliant and noncompliant residues, and the ranges of glyphosate concentrations. Table S5. Distribution of grain-based food (not staple grains) samples in terms of number of samples, number of compliant and noncompliant residues, and the ranges of glyphosate concentrations. Table S6. Distribution of foods for infants in terms of number of samples, number of compliant and noncompliant residues, and the ranges of glyphosate concentrations. Table S7. Distribution of manufactured foods intended for the general population samples in terms of number of samples, number of compliant and noncompliant residues, and the ranges of glyphosate concentrations (PDF)

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