CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1   OVERVIEW

Glyphosate has not been identified in any of the 1,832 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2015). However, the number of sites evaluated for glyphosate is not known.

- Occupational and residential exposure is a result of glyphosate's use in agricultural, industrial, and residential settings. The highest potential for dermal, inhalation, and ocular exposure is expected for pesticide applicators, farm workers, and home gardeners who use herbicides containing glyphosate.

- The general population is exposed to glyphosate via ingestion of crops, plants, and foods with residues of this chemical. Residential exposure may occur via inhalation, dermal contact, and/or ocular contact during mixing or application of consumer products containing glyphosate or by coming into contact with crops, soils, or water to which glyphosate-containing products have been applied.

- Occupational exposure to glyphosate may occur via inhalation, dermal contact, and/or ocular contact during manufacture, transport, mixing, loading, application, and disposal processes. Accidental oral exposure may occur via unintentional ingestion. Dermal contact appears to be the major route of exposure to glyphosate for individuals involved in its application.

- Glyphosate mainly enters the environment as a direct result of its herbicidal use. Fate of this chemical in the environment includes degradation, transport, and partitioning processes, which are governed by its physicochemical properties and by abiotic or biotic degradation under certain environmental conditions. Glyphosate is a nonvolatile, highly polar, non-residual herbicide that has low potential for environmental persistence and is unlikely to bioaccumulate.

5.2   PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1   Production

No information is available in the Toxics Release Inventory (TRI) database on facilities that manufacture or process glyphosate because this chemical is not required to be reported under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986) (EPA 2005b).

Production of glyphosate is achieved through heating phosphorous acid and *a*-amino acetic acid followed by the addition of formaldehyde (Muller and Applebyki 2010). Glyphosate may also be produced by heating glycine and chloromethylphosphonic acid in aqueous sodium hydroxide (IPCS 1994).

Glyphosate is produced commercially in the United States as a technical-grade substance with a purity ≥80%, but usually over 90% (IPCS 1994, McBean 2011).

Glyphosate is typically manufactured for commercial use as a salt available in soluble liquid and soluble granule formulations. Salt forms of glyphosate include the isopropylamine salt, sodium salt, and monoammonium salt. Table 5-1 summarizes some of the common glyphosate salts that may be used as active ingredients in herbicides. Due to the various salt forms, the active ingredient listed on products is sometimes expressed in terms of acid equivalent.

Table 5-1. Glyphosate Salts

Name	CAS Registry Number	EPA PC Code	Cation	U.S. registration[a]
Glyphosate isopropylamine salt	38641-94-0	103601	NH_3^+ / H_3C CH_3	Yes
Glyphosate mono ammonium	40465-66-5	103604	NH_4^+	Yes
Glyphosate ethanolamine salt	40465-76-7	103605	NH_3^+ OH	Yes
Glyphosate triammonium salt	114370-14-8	103607	NH_4^+	Yes
Glyphosate diammonium salt	69254-40-6	103607	NH_4^+	Yes
Glyphosate dimethylammonium salt	34494-04-7	103608	H H N^+ H_3C CH_3	Yes
Glyphosate potassium salts	70901-12-1; 70901-20-1; 39600-42-5	103613	K^+	Yes
Glyphosate monosodium salt	34494-03-6	103603	Na^+	No
Glyphosate sesquisodium salt	70393-85-0	103603	Na^+	No
Glyphosate trimesium	81591-81-3	128501	H_3C S^+ CH_3 CH_3	No

[a]Pan 2014

CAS = Chemical Abstracts Service; EPA = U.S. Environmental Protection Agency; PC = pesticide chemical

Herbicide formulations employing glyphosate salts are commonly produced in combination with additives, inert ingredients, and surfactants. The salt derivatives enhance absorption of glyphosate from the surface of the plant or leaf structure, but are not the herbicidally active portion of the compound. Specific formulations vary in composition and are marketed under numerous trade names (NPIRS 2017; PAN 2009). Polyoxyethylene amine (POEA) (CASRN 24911-53-5) is a surfactant used in the

commercial product Roundup® (PAN 2009). Surfactants are used in herbicide formulations to increase penetration of glyphosate into plants. Sulfuric acid (CASRN 7664-93-9), phosphoric acid (CASRN 7664-38-2), propylene glycol (CASRN 57-55-6), and sodium benzoate (CASRN 532-32-1) are examples of additives used in some formulations (IPCS 1994; PAN 2009). Products may contain other active ingredients such as simazine (CASRN 122-34-9) and 2-methyl-4-chlorophenoxyacetic acid (CASRN 94-74-6). The herbicide 2,4-dichlorophenoxyacetic acid (CAS 94-75-7) may also be present at concentrations ranging from 11.1 to 20.6% (IPCS 1994). Commercial products containing glyphosate have been reported with concentrations ranging from 0.96 to 94 w/w%. The common herbicide, Roundup®, has product formulations containing glyphosate concentrations ranging from 0.96% to 71% (w/w) (NPIRS 2017; PAN 2016b). These products may be diluted depending upon the labeled use as per manufacturers specifications.

The introduction of glyphosate-resistant crops such as soybeans in 1996, canola and cotton in 1997, and maize in 1998, along with the distribution of their genetically engineered seeds, had major impacts on the production and demand for glyphosate.

According to the National Pesticide Information Retrieval System (NPIRS), as of May 2017, there were 43 companies manufacturing EPA federally registered products under the active pesticide code 417300 (glyphosate) (since many chemical names are too long to be handled easily, EPA assigns a 6-digit chemical code number for every active chemical ingredient), which are available for use in the United States; see Table 5-2 (NPIRS 2017). In addition, there were 72 companies in the United States that were manufacturing chemicals under the active pesticide code 103601 (glyphosate isopropylamine salt) (NPIRS 2017).

Table 5-2. Companies Manufacturing Products Under Pesticide Code 417300 (Glyphosate)

Company	Address	City, State, Zip Code
Syngenta Crop Protection, LLC	410 Swing Road	Greensboro, North Carolina 27419
The Scotts Company	D/B/A The Ortho Group, 14111 Scottslawn Road	Marysville, Ohio 43041
FMC Corporation, Agricultural Products Group	1735 Market Street	Philadelphia, Pennsylvania 19103
Monsanto Company	Chesterfield Village Research Center, 700 Chesterfield Parkway North	Chesterfield, Missouri 63017
Winfield Solutions, LLC	P.O. Box 64589	St. Paul, Minnesota 55164

Table 5-2. Companies Manufacturing Products Under Pesticide Code 417300 (Glyphosate)

Company	Address	City, State, Zip Code
ABC Compounding Co., Inc.	P.O. Box 16247	Atlanta, Georgia 30321
Cheminova A/S	P.O. Box 9	DK-7620 Lemvig
Helena Chemical, Co.	225 Schilling Boulevard, Suite 300	Collierville, Tennessee 38017
Chemsico, A Division of United Industries Corporation	P.O. Box 142642	St. Louis, Missouri 63114
Adama Agan Ltd	P.O. Box 262	Ashdod, 77102, Israel
Drexel Chemical Company	P.O. Box 13327	Memphis, Tennessee 38113
Loveland Products, Inc.	P.O. Box 1286	Greeley, Colorado 80632
Nufarm Limited	103–105 Pipe Road	Laverton North, Victoria 3026 Australia
Albaugh, LLC	P.O. Box 2127	Valdosta, Georgia 31604
Atanor S.A.	Foreign Trade Department, Albarellos 4914	B1605 AFR, Munro, Providence de Buenos Aires
BASF Sparks, LLC	P.O. Box 13528	Research Triangle Park, North Carolina 27709
Control Solutions, Inc.	5903 Genoa-Red Bluff Road	Pasadena, Texas 77507
Tenkoz, Inc.	1725 Windward Concourse	Alpharetta, Georgia 30005
Dow AgroSciences, LLC	9330 Zionsville Rd 308/2e	Indianapolis, Indiana 46268
Makhteshim Agan of North America, Inc.	d/b/a Adama, 3120 Highwoods Boulevard, Suite 100	Raleigh, North Carolina 27604
United Phosphorus, Inc.	630 Freedom Business Center, Suite 402	King of Prussia, Pennsylvania 19406
Monsanto Company	Lawn & Garden Products, 600 13th Street, NW, Suite 660	Washington, DC 20005
Helm Agro US, Inc.	401 E. Jackson Street, Suite 1400	Tampa, Florida 33602
Mey Corporation	121 South Estes Drive, Suite 101	Chapel Hill, North Carolina 27514
Sharda Cropchem, Limited	Domnic Holm, 29th Road	Bandra (West), Mumbai 400050
Rotam Agrochemical Company, Ltd.	26/F, E-Trade Plaza, 24 Lee Chung Street	Chaiwan, Hong Kong
Sharda USA LLC	P.O. Box 640	Hockessin, Delaware 19707
Ragan and Massey, Inc.	101 Ponchatoula Parkway	Ponchatoula Louisiana 70454
Tide International, USA, Inc.	21 Hubble	Irvine, California 92618
Agsaver II, LLC	P.O. Box 111	McGehee, Arkansas 71654
Repar-Glypho, LLC	8070 Georgia Avenue, Suite 209	Silver Spring, Maryland 20910
Farmway, Inc.	P.O. Box 640	Hockessin, Delaware 19707
Consus Chemicals, LLC	22 Pine Tree Drive	Wayne, New Jersey 07470
Axss Technical Holdings, LLC	111 Martin Road	Fulton, Mississippi 38843
Cinmax International, LLC	3050 Suite 113	Bloomington, Minnesota 55425

Table 5-2. Companies Manufacturing Products Under Pesticide Code 417300 (Glyphosate)		
Company	Address	City, State, Zip Code
Agromarketing Co., Inc.	133 Mavety Street	Toronto, Ontario, Canada M6P
Glysorttech, LLC	281 Hampshire Drive	Plansboro, New Jersey 08536
Liberty Crop Protection, LLC	4850 Hahns Peak Drive, Suite 200	Loveland, Colorado 80538
Gly-Peak, LLC	224 South Bell Avenue	Ames, Iowa 60010
Tundra Agroindustrial, Ltd.	P.O. Box 10	Lemars, Iowa 51031
Argustoli H.C., LLC	10191 Park Run Drive, Suite 110	Las Vegas, Nevada 89145
Genmerica NA LLC	P.O. Box 1603	Cheyenne, Wyoming
Gruhn Mill Crop Solutions, LLC	701 Fifth Avenue, Suite 6100	Seattle, Washington 98104

Source: NPIRS 2017

5.2.2   Import/Export

No information was found concerning U.S. imports and exports of glyphosate.

5.2.3   Use

Glyphosate is a phosphonoglycine herbicide, first registered for use by the EPA in 1974. In June 1986, glyphosate was issued a Registration Standard (EPA 1986c) requiring additional data, which included phytotoxicity, environmental fate, toxicology, product chemistry, and residue chemistry studies; reregistration of single active ingredient formulations, plus one additional active ingredient formulation, were finalized in 1993 (EPA 1993). Glyphosate is registered for pre- and post-emergent applications for weed control in the production of various fruit, vegetable, and field crops. Glyphosate may be applied to fields prior to planting in order to remove unwanted weeds and vegetation or in preparation for harvesting in glyphosate resistant crops. Recommended application rates, methods of application and timing, temperature considerations, etc. may be found on individual product labels. Glyphosate is in the process of registration review by EPA; docket ID: EPA-HQ-OPP-2009-0361-0066 (EPA 2017c).EPA published an interim registration review decision in January 2020; docket ID: EPA-HQ-OPP-2009-0361 (EPA 2020), which will be finalized after an EPA Endocrine Disruptor Screening Program FFDCA

determination, evaluation of glyphosate under the Endangered Species Act, and the resolution of a petition by the Environmental Working Group.

Glyphosate is used as a non-selective contact herbicide. Formulations are applied directly to control native and invasive weeds and vegetation around food crops and non-food field crops, and in non-crop areas such as roadsides, golf courses, right-of-way locations, and aquatic areas. Glyphosate is used in agriculture, forestry, industrial, lawn and garden, and aquatic (e.g., Rodeo®, Clearcast®) environments for weed control. In aquatic usage, the formulation typically contains no surfactant or a surfactant that is nontoxic to aquatic organisms and applications must be made as per the product instructions to avoid rapid vegetative decay, which can lead to anaerobic environments and potential fish kills (Dow 2017). Glyphosate is applied to control broad-leaved weeds and woody brush, as well as annual and perennial grasses (Muller and Applebyke 2010; Plimmer et al. 2004). The sodium salt (CASRN 34494-03-6) can be used as a plant growth regulator for peanuts and sugarcane (EPA 1993). Glyphosate is a foliar-applied herbicide. Before the introduction of genetically modified glyphosate-resistant crops, application generally occurred before crops were planted (Duke and Powles 2008). After successful production and approval of glyphosate-resistant crops, such as soybean, cotton, maize, and canola, application generally occurs after planting and before harvest; the timing depends on the specific application (Duke and Powles 2008; Muller and Applebyke 2010). The introduction of these glyphosate-resistant crops increased the use of herbicidal products containing this chemical because it is possible to use it post-emergence without actually harming the crop. Greater than 90% of the soybeans produced in the United States are glyphosate tolerant, and most cotton (72%) and about half of the corn (52%) planted in 2007 were glyphosate tolerant (Coupe et al. 2012). It has been estimated that genetically engineered glyphosate-tolerant crops now account for about 56 % of its global usage (Benbrook 2016). Application techniques include aerial treatments, typically used for large-scale purposes, and wiping equipment or spraying equipment attached to vehicles, generally used for small-scale applications (FAO 1997; IPCS 1994). Newer application practices, such as the addition of glyphosate to crops to simplify the harvesting process (referred to as "green burndown"), may have implications for usage rates of the herbicide (Zhang et al. 2019a).
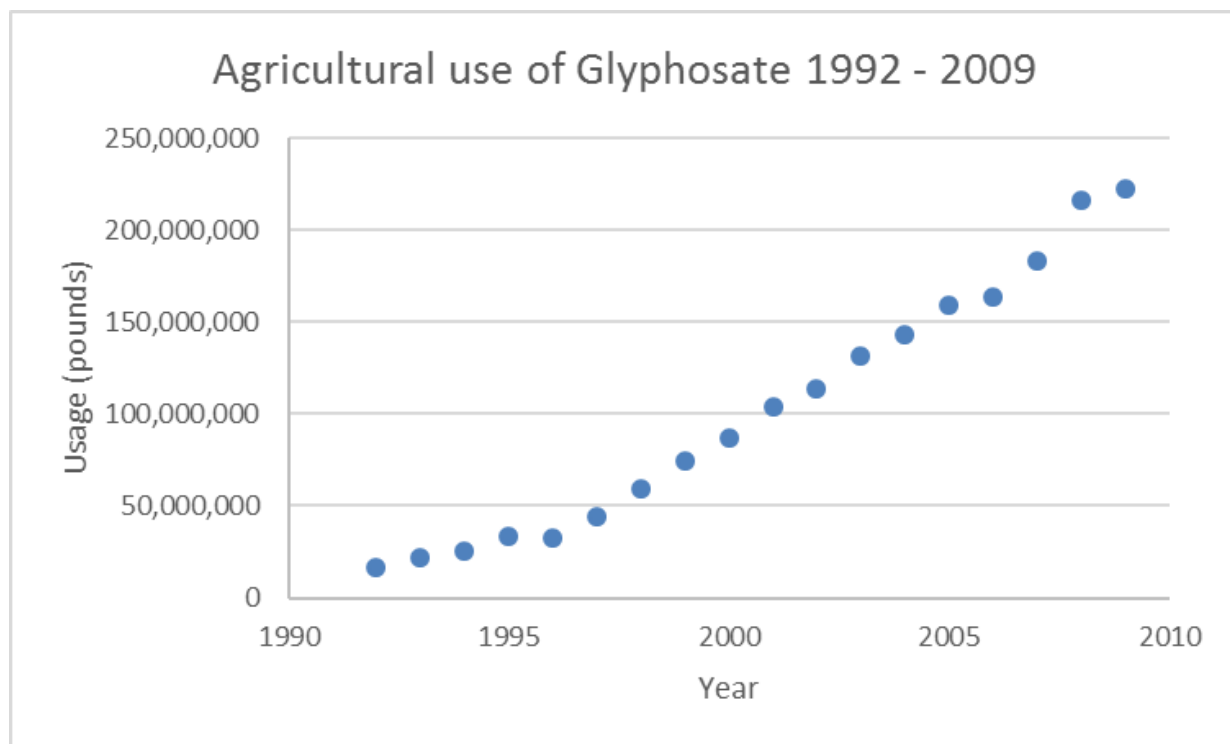
According to data from the Pesticide Action Network (PAN) Pesticide Database, there are 102 products containing glyphosate (CASRN 1071-83-6) as the active ingredient, 94 of which have active registrations in the United States. There are 848 products containing glyphosate isopropylamine salt (CASRN 38641-

94-0) as the active ingredient, of which 739 have active registrations in the United States (PAN 2016a, 2016b).

Increasing trends in annual agricultural use data for the United States are reflected from the use statistics available from the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program. Estimated yearly usage increased from approximately 20 to 60 million pounds from 1992 to 1998, from approximately 70 to 130 million pounds from 1999 to 2003, from approximately 140 to 250 million pounds from 2004 to 2011, and steady use of approximately 285–290 million pounds from 2012 through 2014 (USGS 2017). Figure 5-1 illustrates the agricultural use of glyphosate from 1992 to 2009 in the United States (USGS 2013).

Figure 5-1. Agricultural Application Trends of Glyphosate in the United States According to U.S. Geological Survey (USGS) Data

Source: USGS 2017

Benbrook (2016) compiled data from the National Agricultural Statistical Service (NASS) to estimate the amount of glyphosate applied for weed control in the production of major agricultural crops and non-agricultural (residential uses) in the United States from 1990–2014. The trends are summarized in Table 5-3.

Table 5-3. Glyphosate AI (Pounds) Usage Trends from 1990 to 2014

Crop	1990 Active ingredient (pounds)	2014 Active ingredient (pounds)	% Increase
Soybean	2,663,000	122,473,987	4,499.10%
Corn	880,066	68,949,452	7,734.58%
Cotton	192,429	17,421,787	8,953.62%
Wheat (winter)	331,758	12,353,488	3,623.64%
Alfalfa	381,525	8,853,600	2,220.58%
Sorghum	236,305	4,178,573	1,668.30%
Sugar beets	36,130	2,763,075	7,547.59%
Canola	0	219,392	NA
Wheat (spring)	75,308	1,201,807	1,495.86%
Barley	13,1568	1,064,160	708.83%
Other cops	1,897,522	4,526,043	138.52%
Total	7,683,070	249,906,307	3,152.69%
Non-Agricultural Use			
	5,300,000	26,519,000	400.36%

Source: Benbrook 2016

The EPA recently granted the registration of a new herbicide named Enlist Duo™ containing 2,4-D choline salt and glyphosate for use on genetically modified corn and soybean crops designed to be resistant to 2,4-D and glyphosate (EPA 2014).

5.2.4 Disposal

Wastes resulting from products containing glyphosate should be disposed of at an approved waste disposal facility or in landfills approved for pesticide disposal. Disposal practices should be in accordance with federal, state, and local procedures. Non-refillable containers should never be reused. Empty containers should be rinsed thoroughly and offered for recycling, if available, or disposed of in accordance with container labels. Rinse-water can be emptied into formulation equipment and applied as residual pesticide in the appropriate manner. Do not contaminate fresh waters when disposing of equipment wash waters or container rinse waters. Containers that have not been completely rinsed may be considered hazardous and should be disposed of with regard to federal, state, and local regulations. Any unused product may be recycled by applying the product in an approved use setting or returning it to the manufacturer or supplier for safe disposal (Agrisolutions 2010; EPA 1993, 2011).

5.3   RELEASES TO THE ENVIRONMENT

TRI data should be used with caution because only certain types of facilities are required to report (EPA 2005b). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ ≥10 full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005b).

No information is available in the TRI database on facilities that manufacture or process glyphosate because this chemical is not required to be reported under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986) (EPA 2005b).

The use of glyphosate as an herbicide for crops and non-crop applications is the major source of glyphosate that intentionally enters the environment. Some glyphosate may be released from the manufacture, transport, and disposal of glyphosate or glyphosate-containing products. The majority of herbicidal formulations with glyphosate are directly applied to weeds to remove unwanted vegetation in residential and agricultural settings. Depending on its application, glyphosate may enter aquatic environments through direct application to control aquatic weeds (Dow 2017) or as a result of overspray in areas near aquatic environments. Aerial applications of glyphosate may result in unintended transport, depending on application technique and meteorological conditions, such as wind drift (EPA 1993; IPCS 1994; PAN 2009; Yates et al. 1978).

5.3.1   Air

There is no information on releases of glyphosate to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005b).

Glyphosate released to the air from aerial and ground equipment has the potential for downwind transport. Yates et al. (1978) assessed the loss due to drift after application. The lowest drift losses resulted when ground sprayers operating at low pressure were employed. The highest drift losses occurred when jet nozzles were employed during aerial application performed by helicopter.

The Air Quality System (AQS) database is EPA's repository of criteria air pollutants and hazardous air pollutants (HAPs), containing monitoring data from >2,600 monitoring sites across the United States. Glyphosate has not been included in the AQS ambient air monitoring data as of 2016 (EPA 2017a).

5.3.2   Water

There is no information on releases of glyphosate to water from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005b).

Glyphosate may enter surface water systems either directly as a result of its aquatic use or indirectly due to overspray near surface water. Aquatic applications of glyphosate are used to control invasive aquatic species such as water chestnut (*Trapa natans*) or other labeled weeds (EPA 2010); however, no quantitative data are available regarding how much glyphosate is applied to aquatic waterways in the United States. Glyphosate may also enter surface waters indirectly due to transport of residues in run-off or erosion events. The amount of glyphosate transported to nearby water bodies from runoff and erosion is dependent upon several factors, including the frequency, timing, and application rate of glyphosate to nearby areas, meteorological conditions (e.g., rainfall events and duration), and the characteristics of the soils in the treated areas. Hydrological factors such as input to the waterbody from overland flow as compared to subsurface infiltration also effect potential pesticide loadings. Coupe et al. (2012) studied the glyphosate levels at three locations located in the United States (South Fork River Basin, Iowa; Sugar Creek River Basin, Indiana; and Bogue Phalia Basin, Mississippi). The basins are located in agricultural areas dominated by soybean, corn, rice, and cotton (Mississippi only) production, but have differing climates and soil characteristics. Water samples collected from 2007 to 2008 at three sites located in the Bogue Phalia basin all had detectable levels of glyphosate and its degradation product, aminomethylphosphonic acid (AMPA). Glyphosate concentrations at the sites ranged from 0.03 to 73 µg/L. Levels showed a distinctive seasonal pattern with lowest levels occurring in winter, followed by a steady increase into late fall, which coincided with seasonal application timings of glyphosate. Moreover, both glyphosate and AMPA loads into the basin were greater in 2008 as compared to 2007, which corresponded to a higher rainfall rate for that year. Approximately 59–72% of the water samples

collected from the South Fork River basin had detectable levels of glyphosate ranging from <0.02 to 5.7 µg/L. Higher glyphosate loadings as a percentage of usage into the Bogue Phalia Basin as compared to the South Fork River Basin is a result of a higher overland flow in the basin (as compared to subsurface water infiltration) and the fact that the majority of soils in the Bogue Phalia Basin are characterized as heavy clay soils classified as hydrologic soil groups C and D, which have higher runoff potential than the predominant soil types in the South Fork River Basin.

Glyphosate levels in the Sugar Creek River Basin, Indiana were limited to measurements taken during two heavy rainfall storm events in which 2.6 and 5.7 cm of rain were recorded. Glyphosate levels ranged from 0.16 to 430 µg/L, with the highest level recorded during the heavier rainfall event.

Battaglin et al. (2005) discussed the occurrence of glyphosate in 51 streams in the Midwestern United States from pre-emergence, post-emergence, and harvest runoff samples. Maximum levels in runoff water ranged from 1.00 µg/L (pre-emergence runoff) to 8.7 µg/L in harvest season runoff samples. Glyphosate levels in surface water are summarized in Section 5.5.2.

Aparicio et al. (2013) measured the environmental fate of glyphosate and AMPA in surface water of agriculture basins in Argentina. Forty-two streams were sampled in April, August and September of 2012. Between the collection months, glyphosate was measured in 4% to 35% of samples with levels ranging between trace to 7.6 µg l^{-1}. AMPA was detected in up to 33% of samples collected and concentration levels were measured between non-detect to 2.3 µg l^{-1}. There was a decrease in the number of samples detecting glyphosate or AMPA overtime, and this may be due to the dilution effect caused by rainfall, which was measured as 65.7 mm (April) and 253.5 mm (August) (Aparcio et al. 2013).

5.3.3   Soil

There is no information on releases of glyphosate to soil from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005b).

Glyphosate applied directly to vegetation may migrate to the soil from foliar washoff or translocation from the plants to the root zone. As discussed in Section 5.2.3, glyphosate agricultural uses in the United States increased from about 20 million pounds in 1992 to about 300 million pounds by 2014 (USGS 2017). Battaglin et al. (2014) estimated that nonagricultural uses of glyphosate were about 9,300 metric

tons (20.5 million pounds) in the United States in 2007 and Benbrook (2016) estimated that about
26.5 million pounds were used for nonagricultural purposes in 2014.

A 2008 survey of pesticide application in Ontario, Canada, conducted by the Ministry of Agriculture,
Food, and Rural Affairs reported that glyphosate use increased from an estimated 1,170,762 kg active
ingredient in 2003 up to an estimated 2,062,648 kg active ingredient in 2008 (OMAFRA 2008). A total
of 527,952 kg of glyphosate were used on field crops, 6,700 kg were used on fruit, 6,110 kg were used on
vegetables, and 6,635 kg of glyphosate were used on nursery crops, sod, and ginseng; greenhouse crops
were not included. Specific 2008 glyphosate applications for weed control by crop use amounted to
527,952 kg in production of field corn, 1,253,773 kg for soybean production, 11,087 kg for canola,
155,428 kg for wheat, 9,206 kg for oats, 6,588 kg for barley, 6,167 kg for mixed grains, 3,185 kg for rye,
18,054 kg for white beans, 18,661 kg for dry beans, 27,011 kg for hay, 2,717 kg for pasture, 1,386 kg for
sugar beets, and 1,991 kg for other field crops (OMAFRA 2008).

A 2013/2014 survey of pesticide application in Ontario, Canada, conducted by the Ministry of
Agriculture, Food, and Rural Affairs reported pesticide use for glyphosate (OMAFRA 2015). An
estimated total of 2,909,184 kg of glyphosate were used on all surveyed field crops in 2013/2014; 13,194
kg were used for fruit and 9,869 kg were used for vegetables. Specific crop use in 2013 for the amount of
the active ingredient glyphosate applied as an herbicide equaled 1,151,051 kg for field corn, 1,544,954 kg
for soybeans, 65,230 kg for wheat, 34,573 kg for oats and mixed grains, 11,542 kg for white beans,
27,980 kg for hay and pasture, and 24,144 kg for other field crops (OMAFRA 2015).

5.4   ENVIRONMENTAL FATE

The environmental fate of glyphosate, which includes the transport, partitioning, and transformation of
this substance, is controlled by various physicochemical properties, degradation, and other loss processes.
Glyphosate is a non-volatile, highly polar, non-residual herbicide that has low potential for environmental
persistence and is unlikely to bioaccumulate; the chemical is either degraded or inactivated by adsorption
to soil (Smith and Oehme 1992). Microbial degradation in soils and water is an important fate process;
reported half-lives range from 2 to 215 days in soils and from 1.5 to 130 days in waters (Battaglin et al.
2014; IPCS 1994; PAN 2009; Rueppel et al. 1977). The wide range of half-lives is a result of
environmental conditions such as soil characteristics, pH, and endogenous microbial populations, which
are factors that influence the rate of degradation. Glyphosate is not expected to be susceptible to

hydrolysis; photodegradation has not been confirmed as an important fate process in any environmental media (Smith and Oehme 1992).

5.4.1   Transport and Partitioning

Glyphosate is not expected to change ionic form at pH levels of 5–8 and is expected to exist in its anionic form under most environmental conditions.

Air.   Glyphosate has a low vapor pressure and is expected to exist in the particulate phase in the ambient atmosphere. There is potential for spray drift after application of herbicides, the extent of which is dependent on the mode of application. Aerial applications may result in considerable transport depending on climate conditions (Silva et al. 2018; IPCS 1994; Yates et al. 1978). Drift analysis has shown that 10–37% of applied herbicide can drift to non-target plants. Seedling and plant fatalities were found 20–100 m downwind after application, and residues have been detected at 400 and 800 m downwind following ground and aerial applications, respectively (PAN 2009). Wind erosion is one pathway in which glyphosate and its primary metabolite, AMPA, are transported into the atmosphere; Silva et al. (2018) estimated wind only can contribute between 1941 to 30,000 mg/ ha^{-1} year^{-1} in offsite transport in soils with low to medium and high glyphosate content, respectively (Silva et al. 2018). Furthermore, Bento et al. (2017), reported that glyphosate and AMPA content were highest in the smallest particle sample size (8 µm) tested across three soil types (clay, organic matter, and silt). Glyphosate concentration ranged between 5.5 to 15 µg/g and AMPA content ranged between 0.07 to 0.7 µg/g when particle sizes (8 µm to 715 µm) were analyzed. Because particles <20 µm can be transported in long-term suspension, it's possible that combined with wind speeds, glyphosate particles have the potential to travel long distances and be transported into non-agricultural areas, particularly in conditions where topsoil is sufficiently dry (Bento et al. 2017).

Particulate-phase glyphosate can be removed from the atmosphere by wet or dry deposition. Wet deposition of glyphosate and its major degradation product, AMPA, from the atmosphere ranged from 3.9 to 16 µg/m^2 and from 1.7 to 5.2 µg/m^2, respectively, as reported in a study conducted in Pace, Mississippi, and Blairsburg, Iowa in 2007 and 2008 (Chang et al. 2011). In a study conducted in 2001, the total annual deposition for glyphosate was reported as 49,000 ng/m^2 and the maximum concentration detected was 6,200 ng/L. Glyphosate was detected in about 10% of the collected samples. The total annual deposition for AMPA was reported as 12,757 ng/m^2 and the maximum concentration detected was 1,200 ng/L. The majority of glyphosate detections occurred during the spraying season. Deposition rates

and concentrations of glyphosate were higher at the urban sites; this was attributed to its non-agricultural uses. The concentration of glyphosate and several other herbicides/pesticides were monitored in rainwater in Belgium from 1997 to 2001, and glyphosate was found to have an average annual concentration of 78 ng/L. The concentration increased dramatically during spraying season, reaching a maximum of 6,200 ng/L (Quaghebeur et al. 2004).

Water.   Depending on its application, glyphosate may enter aquatic environments through direct application, or as a result of overspray in areas near aquatic environments .Water erosion is another route in which glyphosate and AMPA are transported into surface water bodies; Silva et al. (2018) estimated water erosion can contribute between 9753 to 47,557 mg/ ha^{-1} year^{-1} in soils with low to medium and high glyphosate content, respectively (Silva et al. 2018). There is evidence of limited run-off and leaching with sandy soils and heavy rainfall (Borggaard and Gimsing 2008). Partitioning into aqueous environments is attenuated by adsorption to soils and sediments.

Sediment and Soil.   Glyphosate will have strong adsorption to most soils due to its ionic nature and is expected to bind to positively charged metal surfaces present in clay and soils. Adsorption occurs through hydrogen bonding ion exchange or complexes of the phosphonate anion as well as the ammonium cation with minerals present in soils (Miles and Moye 1988). In an unpublished report by Monsanto in 1978, <0.1–6.6% of applied activity was recovered in the solution that washed off of the soil columns under leaching conditions simulating a heavy rainfall (IPCS 1994). The potential for run-off and leaching ability of glyphosate was examined by Rueppel et al. (1977) in three soils. Using inclined soil beds and artificial rainfall scenarios, a maximum runoff off <2x10^{-4} kg/ha was reported. Using thin layer chromatography and beta camera analysis, 97–100% adsorption to all three soils indicated that there is minimal possibility for leaching into groundwater. Although glyphosate is expected to adsorb strongly to soil particles and clay minerals, desorption may occur under certain conditions. It has been demonstrated that sorption decreases with increasing soil pH, increasing concentrations of inorganic soil phosphate, and decreasing mineral concentrations (Glass 1987; Gerritse et al. 1996; Piccolo et al. 1994; Plimmer et al. 2004; Smith and Oehme 1992; Sprankle 1975). However, because of the strong sorption to most soils, mobility and the potential for migration into groundwater are low. It is known that glyphosate and AMPA strongly adsorb and accumulate in the top of soils (Silva et al. 2018). The major degradation product, AMPA (CASRN 1066-51-9), also binds to soils and may be more mobile than glyphosate (Duke and Powles 2008; IPCS 1994). Leaching of glyphosate may be possible under certain environmental conditions. In a study examining the environmental fate and leaching risk of aged glyphosate and its metabolite, AMPA, large amounts of glyphosate and AMPA were extracted from soil after treating it with

phosphate solution (to simulate rainwater in the presence of fertilizer) compared to pure water (to stimulate rainwater in non-fertilized soil). The presence of phosphate based fertilizer in soil appears to enhance the probability that glyphosate and its metabolite residue will leach from the soil matrix (Simonsen et al. 2008). While glyphosate and AMPA have been reported to reach shallow groundwater and then transfer to surface water (Grandcoin et al. 2017), the chemical is not expected to leach into groundwater as it is mostly concentrated in the topsoil layers; Glyphosate and AMPA are infrequently detected in deep groundwater systems, and when found, concentrations are generally at low levels (Silva et al. 2018).

Other Media.   Glyphosate is not generally taken up from the soil by a plant's root system since it typically forms bound residues with organic matter in most soils. Absorption of glyphosate via the roots has been discussed in a review by Saunders and Pezeshki (2015); however, many of the studies cited were conducted under hydroponic conditions, which are not likely to be typical of field environments. However, some uptake has been demonstrated to occur under field conditions with low organic-containing soils and in laboratory growing conditions. The EPA Registration Eligibility Decision (RED) document for glyphosate showed that lettuce, carrots, and barley contained glyphosate and AMPA residues after a sandy loam containing 0.3–0.5% organic matter was treated with 3.71 pounds of glyphosate per acre, but accumulation decreased as the length of rotation increased. For example, glyphosate residues were 0.097 ppm in lettuce planted 30 days post-treatment, but only 0.037 ppm in lettuce planted 119 days post-treatment (EPA 1993). After surface application of glyphosate, it may move from the point of application, typically the leaves, to other parts of the plant. In a plant uptake study where glyphosate was aged for 6.5 months in soil before either rape or barley seeds were planted, radioactivity demonstrated translocation of glyphosate into the parts of the plant above the soil after a growth period of 41 days. The measured uptake for rape and barely were equivalent to 14.0 and 11.5 ng/glyphosate/g plant fresh weight, respectively (Simonsen et al. 2008). Glyphosate can be absorbed into the plant or vegetable through its outer wall or skin and can move throughout the stem and leaves of the entire plant. Metabolism of glyphosate within the plant occurs slowly (Doublet et al. 2009; Smith and Oehme 1992; WHO 2005). Glyphosate is mobile inside the plant and may be transported within the phloem system into other tissues before the plant is killed (Duke and Powles 2008; Pankey 2000; Plimmer et al. 2004). Boerboom and Wyse (1988) investigated absorption and translocation of glyphosate using Canada thistle seeds with various concentrations of a formulation of glyphosate (356 g/L) and the surfactant POEA (178 g/L). Translocation from the treated leaf to the root was clearly observed. Translocation generally decreased as the concentration of glyphosate increased. Application of
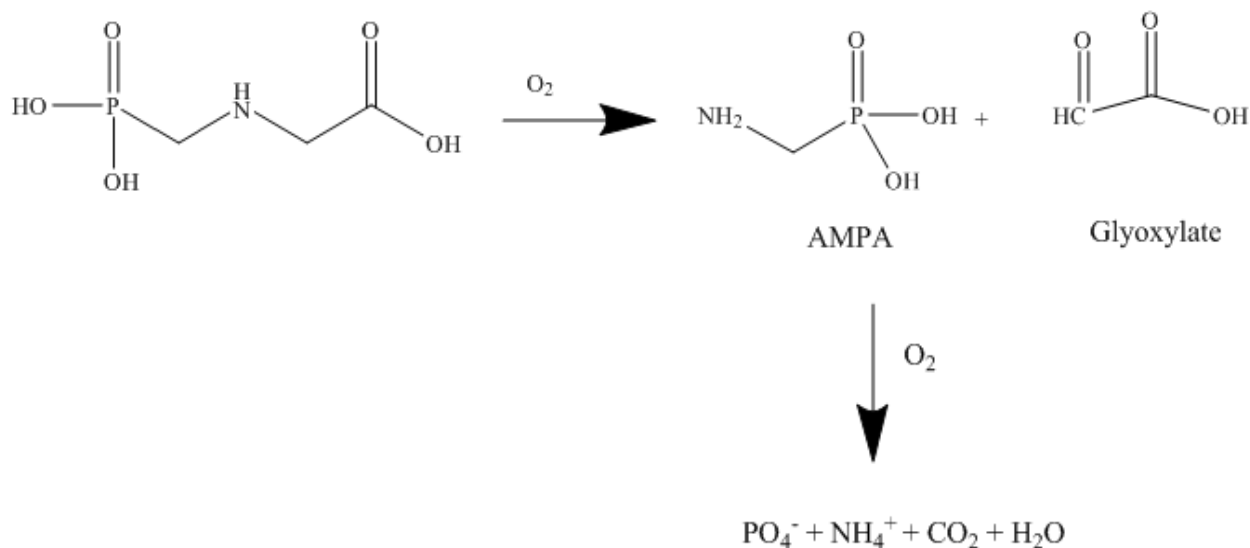
the smaller droplets resulted in greater translocation to the roots compared to application of larger
droplets.

5.4.2   Transformation and Degradation

Glyphosate is readily and completely degraded in the environment mainly by microbial processes.
Microorganisms that degrade glyphosate into its metabolite include *Pseudomonas sp*., *Arthrobacter
atrocyaneus* and *Flavobacterium sp*. (Singh and Singh 2016). Modes of degradation involving glyphosate
oxidoreductase (GOX) and C-Plyase enzymatic pathways have been suggested. AMPA has been
identified as the major metabolite in both soils and water. Sarcosine is an additional degradation product
produced by the C-Plyase enzymatic pathway (Singh and Singh 2016). However, sarcosine has mostly
been found in pure culture experiments, likely due to its fast degradation compared to AMPA (Borggaard
and Gimsing 2008). Glyoxylic acid (CASRN 298-12-4) is an additional degradation product by the GOX
enzymatic pathway. Both pathways result in complete mineralization to inorganic phosphate, carbon
dioxide, ammonium, and water (Balthazor and Hallas 1986; Kishore and Jacob 1987; Shinabarger and
Braymer 1986). AMPA is more persistent than glyphosate and has reported soil half-lives ranging from
32 to 240 days depending on edaphic and environmental conditions such as temperature and soil moisture
(Simonsen et al. 2008; Battaglin 2014; Silva et al. 2018). At colder and drier conditions, degradation of
AMPA is slower (Silva et al. 2018). Aquatic half-lives are similar to glyphosate (Battaglin 2014). Figure
5-2 illustrates the degradation of glyphosate under aerobic conditions.

Figure 5-2. Degradation of Glyphosate Under Aerobic Conditions

Source: Adapted from Schuette 1998

The high water solubility, low log K_{ow}, and ionic nature of glyphosate suggest that this compound would not be expected to bioaccumulate in aquatic organisms (IPCS 1994; WHO 2005). Jackson et al. (2009) measured whole-body bioconcentration factor (BCF) values for glyphosate in bluegill fish (*Lepomis macrochirus*) using EPA guideline method OPPTS 850.1730 for an exposure period of 28 days. A BCF value of 0.52 (log BCF -0.284) was reported, suggesting that bioconcentration was low. Accumulated residues of glyphosate in fish, crustaceans, and mollusks exposed to water containing glyphosate declined approximately 50–90% over 14–28 days after removal from the glyphosate water into glyphosate-free water (WHO 2005). Bioaccumulation of glyphosate in blackworms (*Lumbriculus variegatus*), following soil application of glyphosate and a commercial formulation, was investigated (Contardo-Jara et al. 2009). BCF values after 4 days of exposure to concentrations of 0.05–5 mg/L of both 98% pure glyphosate and the formulation Roundup Ultra® were measured at 20°C (Contardo-Jara et al. 2009). BCF values based on the fresh weight of the worms ranged from 1.2 to 5.9; the BCF values for pure glyphosate at 0.05, 0.5, and 5.0 mg/L were approximately 2.9, 1.1, and 2.8, respectively and BCF values for Roundup Ultra® at 0.05, 0.5, and 5.0 mg/L were approximately 5.9, 3.8, and 2.7, respectively. The greater uptake of glyphosate from the Roundup Ultra® sample was attributed to the surfactant in the formulation, POEA.

The mechanism of action for glyphosate's herbicidal properties involves the inhibition of enzymes in the shikimate pathway. Specifically, the enzyme enolpyruvylshikimate-3-phosphate synthase is inhibited, creating a deficiency of enolpyruvylshikimate-3-phosphate and an abundance of shikimate. It has been suggested that the actual death of the plant is due to the disruption of plant processes regulated by the shikimate pathway essential to plant health and growth such as the primary biosynthesis of aromatic amino acids like phenylalanine, tryptophan, and tyrosine, as well as lignin and chlorophyll, and secondary processes such as flavonoid synthesis. These primary processes are exclusive to plants and some microorganisms and do not occur in any animals; therefore, the inhibition of enzyme production induced by glyphosate only affects species in the plant kingdom. It has also been suggested that the increased carbon flow to the shikimate pathway decreases carbon available for other essential photosynthetic processes (Muller and Applebyke 2010; Pankey 2000; Plimmer et al. 2004; Servaites et al. 1987).

In one version of transgenic plants modified to be glyphosate tolerant, glyphosate is converted to N-acetylglyphosate (CASRN 129660-96-4), a chemical that lacks herbicidal properties (Pioneer 2006). This chemical may be further metabolized to N-acetyl (aminomethyl)phosphonic acid (N-acetyl-AMPA) (PAN 2009). However, the more common method of conferring glyphosate-resistance to plants is promoting the

expression of enolpyruvulshikimate-3-phosphate synthase variants that are resistant to glyphosate-inhibition (Pioneer 2006).

Air.   Glyphosate has low vapor pressure and is considered stable in ambient air. Experimental and monitoring studies have confirmed wind-driven transportation of both glyphosate and AMPA including in areas that never had glyphosate application (Silva et al. 2018; Aparicio et al. 2018).

Water.   Glyphosate is polar, has high water solubility and is expected to exist as an anion at neutral pH (IPCS 1994; O'Neil et al. 2013; Singh and Singh 2016). Based on experimental adsorption coefficients ranging from 8 to 377 dm^3/kg for various soil and clay substrates, glyphosate is expected to adsorb to suspended solids and sediments in water. Precipitation from water has been suggested due to water-insoluble metal complexes with iron(III), copper(II), calcium, and magnesium that have been found; coordination occurs through the amine nitrogen, the carboxylic oxygen, and the phosphate oxygen (Subramaniam and Hoggard 1988). Photodegradation in water is not expected to be an important fate process for glyphosate under environmentally relevant conditions. Experimental half-lives of <28 days upon exposure to natural light have been reported (IPCS 1994; Rueppel et al. 1977). No detectable photodegradation was observed in a study using sterile water and exposure to ultraviolet (UV) light or natural sunlight (Smith and Oehme 1992). Lund-Hoie and Friestad (1986) exposed RoundUp® to UV light at 254 nm at 20°C in the laboratory and exposed 1% RoundUp® solutions in deionized water, polluted water, and water with suspended sediments to natural sunlight (measured λ=295–385 nm) outside at temperatures ranging from 20 to -5°C. Results indicated that photodegradation occurred faster in pure water as opposed to polluted water or water with sediments in which adsorption accounted for the majority of dissipated glyphosate. A photolytic half-life of 3–4 weeks was observed for glyphosate, at an initial concentration of 2,000 ppm in the deionized water exposed to UV light. A photolytic half-life of 5 weeks at 100 ppm was observed for glyphosate in deionized water, exposed to natural sunlight. The rate of hydrolysis is considered very slow. In a study at 35°C, glyphosate did not undergo hydrolysis in buffered solutions with a pH of 5, 7, or 9. Laboratory studies have reported 50% degradation in ≤14 days in water and sediment under aerobic conditions and 14–22 days under anaerobic conditions for glyphosate (IPCS 1994). In an aqueous hydrolysis study at 25°C in buffered solutions of pH 5, 7, and 9, glyphosate was considered hydrolytically stable, with extrapolated half-lives beyond 3 years (EPA Undated).

Rapid dissipation of glyphosate in small forest ponds was observed as a result of sediment sorption and microbial degradation (Goldsborough and Beck 1989). Dissipation in three ponds, pH 5.0–7.7, resulted

in half-lives of 1.5–3.5 days. After 38 days, glyphosate was not detected in any of the samples. AMPA concentrations were consistently low throughout the study.

Microbial degradation of glyphosate in water sediments has been investigated. AMPA has been identified as the major metabolite in water. Rueppel at al. (1977) performed non-sterile and sterile soil/water shake flask experiments to examine the degradation of glyphosate under aerobic and anaerobic conditions. The ^{14}C-labeled glyphosate samples used were between 94.8 and 98.1% pure. Ray silt loam, Norfolk sandy loam, and Drummer silty clay loam soil samples were used. In the sterile soil test, 1.0% degradation was achieved after 7 days; the report suggests that abiotic chemical degradation is not a likely fate process for glyphosate. In non-sterile aerobic and anaerobic tests using Ray silt loam and 14C-labeled glyphosate, 46.8–55.3 and 33.5–51.4% TCO$_2$ (theoretical CO$_2$ evolution), respectively, was achieved after 28 days. In the non-sterile aerobic tests using fresh and bin-stored Drummer loams, just over 40% and just under 20% TCO$_2$, respectively, was achieved after 28 days. In the fresh Drummer loam and Ray loam samples, no lag phases were observed, and the bulk of the degradation occurred by day 7, after which time, the rate of degradation declined. The slowing of degradation was attributed to adsorption to soil. In Ray silt loam and Drummer silty clay loam, degradation of glyphosate reached 90% after 14 and 80 days, respectively, and half-lives were reported as 3 and 25–27 days, respectively. The results were similar at different concentrations of glyphosate. In the non-sterile aerobic test in Norfolk sandy loam, carbon-labeled glyphosate achieved <10% mineralization after 28 days, measured by applied ^{14}C as CO$_2$ evolution, and 43% dissipation occurred after 112 days. A half-life of 130 days was reported for Norfolk soil. The principle degradation product identified, AMPA, was confirmed in soil samples by nuclear magnetic resonance (NMR) imaging, mass spectral analysis, ion-exchange chromatography, and thin-layer chromatography. Minor degradation products identified included N-methylaminomethylphosphonic acid, glycine, N,N-dimethylaminomethylphosphonic acid, and hydroxymethylphosphonic acid, all of which were typically present at <1% (Rueppel et al. 1977). The metabolite, AMPA, achieved 16.1 and 34.8% degradation after 63 days in Drummer and Ray loams, respectively, measured by applied ^{14}C as CO$_2$ evolution.

Abiotic degradation was examined by Ascolani Yael et al. (2014) in aqueous solution in the presence of copper salts; results indicated that glyphosate interactions with metal ions in soils may catalyze degradation to AMPA. Further investigation was proposed.

Sediment and Soil.   Glyphosate is readily degraded in the terrestrial environment by a variety of microorganisms. Bacteria, actinomycetes, fungi, and other soil microbes have the ability to degrade

glyphosate. AMPA has been identified as the major metabolite in soil. Glyphosate may also be degraded in soil to sarcosine and inorganic phosphate. Photodegradation is not expected to be an important fate process in soil.

After application of Roundup® at about 2.0 kg/ha (acid equivalent of isopropylamine salt of glyphosate) to Carnation Creek watershed (10 km^2 study area), 50% of the glyphosate residues in soil dissipated after 45–60 days and 82–94% dissipated after 360 days (Feng et al. 1990a).

It has been demonstrated that inorganic phosphate present in soils may inhibit some microbial degradation of glyphosate (Kishore and Jacob 1987). Strains capable of using glyphosate as a sole carbon, nitrogen, or phosphorus source, thereby degrading glyphosate, include *Flavobacterium* sp. (Balthazor and Hallas 1986), which is known to degrade glyphosate in the presence of phosphate, *Pseudomonas* sp. PG2982 (Kishore and Jacob 1987; Shinabarger and Braymer 1986), *Arthrobacter atrocyaneus* (Pipke and Amrhein 1988), and *Rhizobium* spp. (Liu et al. 1991). Biodegradation may involve co-metabolism with other energy sources as well (Sprankle et al. 1975). Degradation products include AMPA and glyoxylic acid, which are subsequently degraded to inorganic phosphate, carbon dioxide, and ammonium. In addition, some bacterial degradation results in the production of sarcosine and inorganic phosphate (Borggaard and Gimsing 2008; Kishore and Jacob 1987; Liu et al 1991; Pipke and Amrhein 1988; Shinabarger and Braymer 1986).

Microbial degradation of bound and unbound glyphosate in several soils resulted in 17.4–45% ultimate degradation after 28 days; the highest degradation rate was observed in Conover sandy clay loam soil (Sprankle et al. 1975). The majority of the degradation was attributed to co-metabolic processes of soil microbes, with possible chemical degradation occurring.

In a biodegradation experiment with activated sludge, the bacterial strain, *Flavobacterium* sp., was identified as the microorganism metabolizing glyphosate to AMPA. This degradation was followed by complete mineralization of AMPA, using the enzyme phosphonatase, to carbon dioxide (CO_2), phosphate (PO_4^{3-}), ammonium (NH^{4+}), and water (H_2O) (Balthazor and Hallas 1986).

A variety of microorganisms are capable of degrading glyphosate. In one degradation pathway, the initial step involves cleavage of the carbon-phosphate bond to produce sarcosine and inorganic phosphate. This is followed by conversion of sarcosine to glycine and formaldehyde. *Pseudomonas* sp. PG2982 uses the enzyme, C-P lyase, to cleave the carbon-phosphate bond in glyphosate, producing sarcosine. This is

followed by the cleavage of sarcosine into glycine and formaldehyde (Kishore and Jacob 1987; Shinabarger and Braymer 1986). Glycine and formaldehyde are metabolized in other biosynthesis processes, such as the oxidation of formaldehyde to carbon dioxide. Multiple strains in the bacterial family *Rhizobiaceae* have the ability to metabolize glyphosate. Liu et al. (1991) found that rhizobia bacterial cells took up close to 85% of available glyphosate within 30 minutes, after which time, the percentage began to decrease. Thin layer chromatography confirmed the presence of sarcosine and glycine as degradation products.

Doublet et al. (2009) studied the degradation of plant absorbed glyphosate in soils. Plants containing residues of glyphosate can enter the soils during crop cycling or harvesting. Degradation of glyphosate was different depending on the plant tissue in which it was absorbed. Mineralization rate constants (k (day^{-1})) ranged from 0.031 to 0.097 in the apex of oilseed rape and in the lamina of maize, respectively. It was noted that absorption of glyphosate in plants delayed degradation in soil.

Glyphosate is expected to adsorb strongly to soil particles and clay minerals; however, the amount of glyphosate sorbed decreases with increasing soil pH. Adsorption and desorption of glyphosate were examined using HPLC (Gerritse et al. 1996; Glass 1987; Piccolo et al. 1994; Sprankle et al. 1975). Adsorption to agricultural soils and clay minerals and the effects of pH and cation saturation were examined by Glass (1987). The K_{oc} values were 4,900 for clay loam with pH 7.5 and organic content (OC) of 1.56%; 3,400 for silt loam with pH 5.8 and OC of 1.64%; and 2,600 for sandy loam with pH 5.6 and OC of 1.24%. The adsorption and desorption of glyphosate and the effects of soil characteristics in four various soil types were assessed (Piccolo et al. 1994). Some characteristics for the four soils follow: Sample A, pH 8.0 and 0.00 OC % (64.1% silt); sample B, pH 5.8 and 3.73 OC% (46.3% sand); sample C, pH 4.6 and 9.23 OC % (81.5% sand); and sample D, pH 8.3 and 0.45 OC % (82.4% silt). The greatest adsorption occurred in the soil with the highest concentrations of iron (4.74%) and aluminum (1.57) oxides (sample B); the greatest desorption occurred in the soil with lowest concentration of iron (0.18%) and aluminum (0.16%) oxides (sample A). The percent desorptions of glyphosate from the four soils were 81% in sample A, 15% in sample B, 72% in sample C, and 35% in sample D. A ligand exchange mechanism is hypothesized for the adsorption of glyphosate involving either the phosphonic component or the carboxylic component of this substance and adsorption to iron and aluminum sites (Benetoli et al. 2010; Piccolo et al. 1994). The adsorption and desorption of both glyphosate and its metabolite, AMPA, were examined by Gerritse et al. (1996) using five soil types. K_{oc} values calculated for soil organic carbon ranged from 8.5 to 5×10^6 after 1 day and from 45 to $>5 \times 10^6$ after 1 week. The strongest adsorption occurred in the soil with the highest iron and aluminum content. The weakest adsorption

occurred in the soil with the highest organic content. These results indicate that glyphosate has a notable affinity towards some soils, particularly with lower pH values and greater mineral content, and desorption occurs under certain environmental conditions especially as pH values increase and mineral concentrations decrease. The EPA CompTox Chemicals Dashboard provided a predicted K_{oc} range of 0.00169–2,080 L/kg, which again indicates a range of mobility in soil likely determined by affinity towards these soil properties.

During a monitoring study with mixtures of Roundup® plus an additional herbicide, soil adsorption and desorption studies were performed on soils from Baton Rouge, Bridge City, and Hammond Louisiana (LaDOTD 1995). The Hammond soil with a pH <8 adsorbed >90% of the applied glyphosate. Adsorption values (Kf) were 8.7, 0.1, and 0.34 for Baton Rouge, Bridge City, and Hammond soils, respectively. Desorption values (Kd) were 355, 0.04, and 0.005 µg/g for Baton Rouge, Bridge City, and Hammond soils, respectively.

Greater than 90% of the glyphosate residues detected in forest soil samples (pH 4.20–5.28), where herbicides containing glyphosate had been sprayed, were found in the upper layers (depth of 0–15 cm) of the soils in both seasonally flooded and well-drained soils, indicating minimal leaching of glyphosate (Feng et al. 1990b).

Glyphosate dissipates from soil under certain environmental conditions. Half-life values between 2 and 215 days have been reported (Battaglin et al. 2014). In field experiments, dissipation from the soil due to run-off has been demonstrated (IPCS 1994). Landry et al. (2005) examined the leaching potential and mineralization of glyphosate in vineyard soils by monitoring outdoor soil columns from May 2001 to May 2002. Bare and grass-covered soils with pH values ranging from 8.0 to 8.4 were studied. Sand, silt, and clay contents were 23.8–34.4, 36.5–39.6, and 29.1–36.9%, respectively, of the bare soils and 26.2–35.6, 34.2–41.3, and 29.6–32.5%, respectively, of grass-covered soils. An aqueous solution of herbicide containing 340 mg/L glyphosate was applied to both soil column surfaces. Effluents from the bare and grass-covered soils were collected weekly and after heavy precipitation to evaluate leaching of glyphosate and AMPA. Glyphosate was detected in 37% of the bare soil leachates and 27% of the grass-covered soil leachates. The highest concentrations measured from the bare soil leachate and grass-covered leachate were 17 and 2.7 µg/L, respectively. AMPA was detected in 90% (maximum concentration 9.4 µg/L) of the bare soil leachates and 41% (maximum concentration 3.5 µg/L) of the grass-covered soil leachates. Mineralization analysis was performed at 20°C for 42 days in both soils. In the grass-covered soil and bare soil, ^{14}C-labeled glyphosate achieved 46.5 and 43.5% CO_2 evolution after 42 days, respectively.

Rapid degradation was observed with no lag phase; the highest rate of degradation occurred within the first 2 days. It was suggested that the initial rapid degradation was based on the degradation of free glyphosate and slowing rates of degradation were attributed to the degradation of adsorbed glyphosate.

Other Media.   After application of herbicides, 30–97% of the applied glyphosate may be taken up by the plant by absorption from the treated leaves. Glyphosate-based formulations containing surfactants (and adjuvants) have a higher rate of absorption compared to glyphosate water solutions (Doublet et al. 2009). Surfactants in herbicide formulations aid in the adsorption and absorption of the active ingredient. Glyphosate is absorbed by plant foliage and transported or moved through the plant via phloem vessels; translocation patterns depend on the specific species of plant. Glyphosate enters these vessels slowly, but once inside, it becomes 'trapped' because of the pH within the vessels, which causes ionization (Gomes et al. 2014; IPCS 1994). Glyphosate may be degraded or metabolized in plants, AMPA is a notable degradation product (Duke 2011). An examination of the metabolism of glyphosate in soybean and canola suggest that some plants use a GOX enzyme for the conversion of glyphosate to AMPA. Degradation of glyphosate in glyphosate-resistant crops may give a better picture of the metabolic processes without interferences found in conventional crops. In transgenic plants modified to be glyphosate tolerant, glyphosate is converted to N-acetylglyphosate, which lacks herbicidal properties (Pioneer 2006). This chemical may be further metabolized to N-acetyl-AMPA (PAN 2009). Glyphosate and AMPA accumulate less in glyphosate-resistant crops than in conventional crops. Lower glyphosate and AMPA levels in glyphosate-resistant canola compared to conventional crops suggested that metabolism is more rapid in glyphosate-resistant canola (Duke 2011).

5.5   LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to glyphosate depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of glyphosate in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on glyphosate levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

Table 5-4 shows the lowest limits of detection (LODs) that are achieved by analytical analysis in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-5.

Table 5-4. Lowest Limit of Detection Based on Standards[a]

Media	Detection limit	Reference
Air	0.01 ng/m^3	Chang et al. 2011
Drinking water	5.99 µg/L (ppb)	EPA 1990
Surface water and groundwater	Glyphosate and AMPA 0.02–0.10 µg/L 0.005 µg/L	Lee et al. 2002; USGS 2002 Ibanez et al. 2005
Soil and sediment	Organic soil =0.05 µg/g Mineral soil=0.02 µg/g Foliage=0.10 µg/g Sediment=0.03 µg/g Soil=0.005 µg/g	Thompson et al. 1989 Ibanez et al. 2005
Whole blood	15 ng/mL	Aris and LeBlanc 2011
Urine	0.09 ng/mL 0.1 ng/mL	Biagini et al. 2004 Jensen et al. 2016
Milk (human and bovine)	10 µg/L (ppb)	Jensen et al. 2016
Crops and commodities	0.01 mg/kg	Alferness 1993

[a]Detection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

AMPA = aminomethylphosphonic acid

Table 5-5. Summary of Environmental Levels of Glyphosate

Media	Low	High	For more information
Outdoor air (ng/m^3)	<0.01 (glyphosate) <0.01 (AMPA)	9.1 (glyphosate) 0.97 (AMPA)	Table 5-6
Surface water (ppb)	0.02	427	Table 5-8
Ground water (ppb)	0.01	4.7	Table 5-9
Drinking water (ppb)	Not detected		Table 5-9
Food (ppb)	0.078	5.47	Section 5.5.4, Other Media
Sediment	Not detected		Table 5-10

AMPA = aminomethylphosphonic acid

A study by the USGS evaluated 3,732 environmental samples across 38 states and the District of Columbia from several studies examining glyphosate in the environment; the samples were collected between 2001 and 2010 from 1,341 different sites, including groundwater; lakes, ponds, and wetlands; soil water; streams; large rivers; precipitation; ditches and drains; soil and sediment; and waste water treatment plant outfall (Battaglin et al. 2014). Glyphosate was detected in 39.4% of all the samples, with a median value of <0.02 µg/L and a maximum value of 476 µg/L. Its degradation product, AMPA, was detected in 55% of all the samples, with a median value of 0.04 µg/L and a maximum value of 397 µg/L.

Groundwater (n=1,171) had the smallest percentage of detections, with 5.8% for glyphosate and 14.3% for AMPA. Glyphosate was detected in 53% of the 1,508 stream samples and AMPA was detected in 72%. Glyphosate was detected in 34% and AMPA was detected in 30% of the 104 small body water samples such as lakes and ponds. Out of 11 wastewater treatment plant (WWTP) samples, glyphosate and AMPA were detected in 9.1 and 82%, respectively. Out of 85 precipitation samples, glyphosate was detected in 71% and AMPA was detected in 72%. Glyphosate was detected in 71% of the 374 ditch and drain samples, with a median value of 0.02 µg/L and a maximum value of 427 µg/L. Glyphosate was only detected without its degradation product, AMPA, in 2.3% of all of the samples; AMPA was detected without glyphosate in 17.9% of the samples. In 42.7% of all of the samples, neither analyte was detected. Several sites with multiple samples during the years 2001–2005 and 2006–2010 indicated that the detection frequency and median concentration of both glyphosate and AMPA had increased in the environment (Battaglin et al. 2014). The highest level of glyphosate was detected in soils and sediments. Out of 45 samples, glyphosate was detected in 91%, with a median value of 9.6 µg/kg and a maximum value of 476 µg/kg. AMPA was detected in 93.3% of 45 samples, with a median value of 18 µg/kg and a maximum value of 341 µg/kg.

5.5.1 Air

Ambient air monitoring data for glyphosate are compiled in Table 5-6.

Table 5-6. Outdoor Air Monitoring Data for Glyphosate

Location	Date	Median concentration (range) in ng/m^3	Notes	Reference
Agricultural ambient air; Mississippi	2007	Glyphosate: 0.48 (<0.01–9.1) AMPA: 0.06 (<0.01–0.49)	Glyphosate and AMPA detected in 19/22 air samples	Chang et al. 2011
	2008	Glyphosate: 0.24 (<0.01–1.5) AMPA: 0.02 (<0.01–0.09)	Glyphosate and AMPA detected in 27/27 and 19/27 air samples, respectively	
Agricultural ambient air; Iowa	2007	Glyphosate: 0.08 (<0.01–5.4) AMPA: 0.02 (<0.01–0.97)	Glyphosate and AMPA detected in 11/18 and 10/18 air samples	Chang et al. 2011
	2008	Glyphosate: 0.22 (<0.01–7.7) AMPA: 0.04 (<0.01–0.38)	Glyphosate and AMPA detected in 13/18 and 11/18 air samples	
Agricultural breathing zones; Baton Rouge, Bridge City,	June 19, 1990– October 9, 1990	<0.1–138.6 µg/m	Breathing zone air (110 samples); sampled in areas where mixtures of commercial herbicides were applied using spray equipment with operating capabilities of 0.37 L/minute	LaDOTD 1995

Table 5-6. Outdoor Air Monitoring Data for Glyphosate

Location	Date	Median concentration (range) in ng/m³	Notes	Reference
Hammond, Louisiana;				

AMPA = aminomethylphosphonic acid

5.5.2   Water

A comprehensive study conducted by the USGS from 2001 to 2006 examined glyphosate and its degradation product, AMPA, in 2,135 groundwater and surface water samples, 14 rainfall samples, and 193 soil samples in major river basins in the United States (USGS 2007). Results indicated that AMPA was detected more frequently and at similar concentrations than parent glyphosate in many samples. The results are summarized in Table 5-7.

Table 5-7. Glyphosate and its Degradation Products in Water Samples in Major U.S. River Basins

N		Glyphosate				AMPA	
	Detections	Maximum (µg/L)	Minimum (µg/L)	Detections	Maximum (µg/L)	Minimum (µg/L)
			Groundwater				
873	68	4.7	0.02	133	2.6	0.02
			Surface water				
1,262	489	427	0.02	725	41	0.02
			Rainfall				
14	12	1.1	0.3	12	0.47	0.02

Source: USGS 2007

Additional water monitoring data for glyphosate are compiled in Tables Table 5-8 and Table 5-9.

5.5.3   Sediment and Soil

Sediment and soil monitoring data for glyphosate are compiled in Table 5-10.

5.5.4   Other Media

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In 2006, 20 prepared food samples were examined for glyphosate residues using electrospray ionization–
liquid chromatography tandem mass spectrometry with limit of quantitation of 0.01 mg/kg and an LOD of
0.005 mg/kg (McQueen et al. 2012). Composite food samples assessed had a mean concentration of
0.08 mg/kg.

Four weeks post application of glyphosate at 4.5 kg/ha to separate pots planted with conventional corn,
cotton, soybeans, and wheat, concentrations of glyphosate were 0.21, 0.26, 0.20, and 0.20 mg/kg,
respectively. Six weeks after application, concentrations in corn, cotton, soybeans, and wheat were 0.14,
0.21, 0.29, and 0.18 mg/kg, respectively, and 8 weeks after application, concentrations in corn, cotton,
soybeans, and wheat were 0.079, 0.42, 0.076, and 0.35 mg/kg, respectively (FAO 2005). Four-week
concentrations of glyphosate in control crops of corn, cotton, soybeans, and wheat were 0.068, 0.04,
0.029, and 0.008 mg/kg, respectively. Six-week concentrations in control crops of corn, cotton, soybeans,
and wheat were 0.089, 0.020, 0.11, and 0.015 mg/kg, respectively, and 8-week concentrations in control
crops of corn, cotton, soybeans, and wheat were 0.022, 0.27, 0.045, and 0.061 mg/kg, respectively (FAO
2005).

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Table 5-8. Surface Water Monitoring Data for Glyphosate

Location	Date	Concentration (range) in µg/L	Notes	Reference
Surface water United States	2016	Mean: 0.30 ; Median 0.10; (0.02–5.1)	EPA STORET data: Routine monitoring samples from USGS Science Centers in Arkansas, California, Colorado, Connecticut, Georgia, Idaho, Illinois, Indiana, Iowa, Kansas, Kentucky, Louisiana, Michigan Center, Maryland, Massachusetts, Minnesota, Mississippi, Missouri, Montana, Nebraska, Nevada, New Jersey, New Mexico, New York, North Carolina, North Dakota, Oregon, South Carolina, Texas, Utah, Washington, and Wyoming	WQP 2017
Surface water United States	2015	Mean: 0.27; Median 0.08; (0.02–24.20)	EPA STORET data: Routine monitoring samples from Minnesota Department of Agriculture–Pesticide and USGS Science Centers in Alabama, Arizona, Arkansas, California, Colorado, Connecticut, Georgia, Idaho, Illinois, Indiana, Iowa, Kansas, Kentucky, Louisiana, Maryland, Massachusetts, Michigan Center, Minnesota, Mississippi, Missouri, Montana, Nebraska, Nevada, New Jersey, New Mexico, New York, North Dakota, North Washington, Ohio, Oklahoma, Oregon, South Carolina, South Dakota, Texas, Utah, Washington, and Wyoming	WQP 2017
Surface water United States	2014	Mean: 0.38; Median 0.10; (0.02–8.10)	EPA STORET data: Routine monitoring samples from Minnesota Department of Agriculture–Pesticide and USGS Science Centers in Alabama, Arizona, Arkansas, California, Colorado, Connecticut, Florida, Georgia, Hawaii, Idaho, Illinois, Indiana, Iowa, Kansas, Kentucky, Louisiana, Maryland, Massachusetts, Michigan, Minnesota, Mississippi, Missouri, Montana, Nebraska, Nevada, New Jersey, New Mexico, New York, North Carolina, North Dakota, Ohio, Oklahoma, Oregon, Pennsylvania, South Carolina, Texas, Utah, Virginia, Washington, and Wyoming	WQP 2017
Surface water United States	March to October 2013	Mean: 0.85; Median 0.34; (0.02–27.80)	EPA STORET data: Routine monitoring samples from Minnesota Department of Agriculture and USGS Science Centers in Idaho, Illinois, Indiana, Iowa, Kansas, Kentucky, Minnesota, Missouri, Nebraska, New York, North Carolina, Ohio, South Dakota, Wisconsin, and Wyoming	WQP 2017

Table 5-8. Surface Water Monitoring Data for Glyphosate

Location	Date	Concentration (range) in µg/L	Notes	Reference
Rivers, small streams, agricultural ditches, and low-flow wetlands Southern Ontario	May and mid-December 2004; April and November 2005	5–41	2004: 203 surface water samples collected from 26 sites 2005: 299 samples taken from 58 sites ~50% of sites detected glyphosate multiple times AMPA detected at trace levels (20–66 µg/L in 5.4% of samples)	Struger et al. 2008
Streams Minnesota, Wisconsin, Nebraska, Iowa, Illinois, Indiana, Ohio, Kansas, and Missouri	2002	Minimum: 0.10–0.46 detected in Iowa, Missouri, and Wisconsin Maximum: 0.54–8.7 detected in Illinois, Indiana, Kansas, Minnesota, Nebraska, and Wisconsin	51 locations (155 total samples); samples collected post-application of pre-emergence herbicides, post-application of post-emergence herbicides, and during the harvest season. Glyphosate detected at levels above the method reporting limit of 0.10 µg/L in 35% of pre-emergence samples, 40% of post-emergence samples, and 31% of harvest season samples. AMPA detected at levels >0.10 µg/L in 53% of pre-emergence samples, 83% of post-emergence samples, and 73% of harvest season samples.	Battaglin et al. 2005
Drainage basins for surface-water or rainwater sampling sites from multiple USGS studies in Florida, Georgia, Illinois, Iowa, Kansas, Mississippi, Nebraska, South Dakota, Vermont, and Washington	2001 through 2006	0.02–427 in surface water 0.3–1.1 in rainwater	Glyphosate and AMPA measured in 1,262 surface water samples and 14 rainwater samples. Glyphosate detected in 489 surface water samples and in 12 rainwater samples. AMPA detected in 725 surface water samples and 12 rainwater samples.	USGS 2007

Table 5-8. Surface Water Monitoring Data for Glyphosate

Location	Date	Concentration (range) in µg/L	Notes	Reference
Rainwater Mississippi	2007	Glyphosate: Median: 0.2 (<0.1–1.9) AMPA: Median: 0.1 (<0. 1–0.3)	Glyphosate and AMPA detected in 8/11 and 8/11 samples, respectively	Chang et al. 2011
	2008	Glyphosate: Median: 0.15 (<0.1–1.6) AMPA: Median: <0.1 (<0. 1–0.48)	Glyphosate and AMPA detected in 13/11 and 14/19 samples, respectively	
Rainwater Iowa	2007	Glyphosate: Median: 0.2 (<0.1–2.5) AMPA: Median: <0.1 (<0. 1–0.2)	Glyphosate and AMPA detected in 10/14 and 5/14 samples, respectively	Chang et al. 2011
	2008	Glyphosate: Median: 0.1 (<0.1–1.8) AMPA: Median: <0.1 (<0. 1–0.24)	Glyphosate and AMPA detected in 15/24 and 12/24 samples, respectively	
Rainwater Indiana	2004	Glyphosate: Median: 0.14 (<0.1–1.1) AMPA: Median: <0.1 (<0.1–47)	Glyphosate and AMPA detected in 11/12 and 11/12 samples, respectively	Chang et al. 2011
Rainwater Flanders, Belgium	2001	Maximum during spraying season: Glyphosate: 6,200 ng/L AMPA: 1,200 ng/L Average annual concentrations: Glyphosate: 78 ng/L AMPA: 20 ng/L	Glyphosate detected in 10% of samples; AMPA detected in 13% of samples	Quaghebeur et al. 2004
Streams of Southeast Buenos Aires, Argentina	2012	Glyphosate: 0.5 µg/L – 7.6 µg/L AMPA: non-detect to 2.3 µg/L	Glyphosate detected in 35%, 10% and 4% samples collected in April, August and September, respectively. AMPA detected in 33% and 7%, of samples in April and August, respectively. AMPA was not detected in samples collected in September.	Aparicio et al. 2013
Gualeguay or Gualeguaychu River, Argentina	2012	Glyphosate: 0.73 µg/L AMPA: 0.53 µg/L	Glyphosate detected in 3/11 samples; AMPA detected in 6/11 samples.	Primost et al. 2017

AMPA = aminomethylphosphonic acid; EPA = U.S. Environmental Protection Agency; MDL = method detection limit; STORET = STOrage and RETrieval; USGS = U.S. Geological Survey

Table 5-9. Groundwater Monitoring Data for Glyphosate

Location	Date	Concentration (µg/L)	Notes	Reference
Drainage basins for surface-water or rainwater sampling sites from multiple USGS studies in Florida, Georgia, Illinois, Iowa, Kansas, Mississippi, Nebraska, South Dakota, Vermont, and Washington	2001 through 2006	0.02–4.7	Glyphosate and AMPA measured in 873 groundwater samples. Glyphosate detected in 68 groundwater samples, and AMPA detected in 133 groundwater samples.	USGS 2007
Groundwater Wyoming	September 9, 2010	1.6	EPA STORET data: Routine monitoring sample from USGS Wyoming Water Science Center	WQP 2017
Groundwater Florida	March 2, 2010	0.14	EPA STORET data: Routine monitoring sample from USGS Florida Water Science Center	WQP 2017
Groundwater Louisiana	April, October, and November 2011	0.03–2.2	EPA STORET data: Routine monitoring sample from USGS Louisiana Water Science Center; depths 43.5–82 feet	WQP 2017
Groundwater Alabama Texas	February and April, 2012	0.01–0.06	EPA STORET data: Routine monitoring sample from USGS Alabama Water Science Center; USGS Texas Water Science Center	WQP 2017
Groundwater Kansas	June and August 2014, June 2015, July 2016	0.02–0.24	EPA STORET data: Routine monitoring sample from USGS Kansas Water Science Center	WQP 2017

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Table 5-9. Groundwater Monitoring Data for Glyphosate

Location	Date	Concentration (µg/L)	Notes	Reference
Groundwater 23 U.S. states	2001–2010	Median: <0.02 Maximum: 2.03	Detected in 68 out of 1,171 samples	Battaglin et al. 2014
Groundwater Washington, DC	2008	0.02	Detected in 1 out of 13 well; not detected in 14 wells sampled in 2005	USGS 2010
Well water Minnesota	October and November 2014, 2015	Not detected	EPA STORET data: Routine monitoring sample from Minnesota Department of Agriculture Pesticide Monitoring Program; activity depth reported at 0 m	WQP 2017
Aquifer, Mesopotamia Pampas, Argentina	January and March 2012	Not detected	Ground water collected from pump 40 to 60 meter deep aquifer	Primost et al. 2017

EPA = U.S. Environmental Protection Agency; STORET = STOrage and RETrieval; USGS = U.S. Geological Survey

Table 5-10. Sediment and Soil Monitoring Data for Glyphosate

Location	Date	Concentration (µg/g)	Notes	Reference
Sediment Big Valley Rancheria, California	July 6, 2010	Not detected	EPA STORET data: Routine monitoring samples from Big Valley Band of Pomo Indians of the Big Valley Rancheria, California: two samples; depth: 0.152 m; MDL: 0.017 mg/kg	WQP 2017
Soil and sediment Indiana, Mississippi	2001–2010	Median: 0.0096; maximum: 0.476	Detected in >90% of 45 samples	Battaglin et al. 2014
Estuary Willapa Bay, Washington	July 1997– 1999	1997 mudflat samples: 2.58–16.3 1998 mudflat samples: 3.11–9.94 1999 mudflat samples: 0.311–1.21 1997 meadow samples: 0.090–0.265 1998 meadow samples: 0.163–2.30 1999 meadow samples 0.472–1.32 (dry weight)	Aqueous herbicide formulated with Rodeo (5% solution v/v) and LI-700 (2% solution) applied in mudflat and cordgrass plots of land in 1997 and 1998	Kilbride and Paveglio 2001
Major river basins in the United States	2011–2006	193 samples collected; 119 glyphosate detections (0.001–0.476); 154 detections AMPA, (0.001–0.956)	Samples collected as part of USGS study	USGS 2007
Streams Southeast Buenos Aires, Argentina	September 2012	Glyphosate minimum: 5.7 µg/kg; maximum: 221.2 µg/kg AMPA minimum: 5.1 µg/kg; maximum: 235 µg/kg	Glyphosate was detected in 66% of samples from 44 streams in Southeast Buenos Aires AMPA was found in 89% of samples from 44 streams in Southeast Buenos Aires	Aparicio et al. 2013
Soils of Southeast Buenos Aires, Argentina	September 2012	Glyphosate: 35 to 1502 µg/kg AMPA: 299 to 2256 µg/kg	Sixteen farms were selected for soil sampling in the southeast of the Province of Buenos Aires where glyphosate had been used	Aparicio et al. 2013
Los Frentones (Chaco), Argentina	November 2004 to November 2010	Glyphosate: 2.4 µg/kg AMPA: 6.3 µg/kg	Soil analysis conducted in semiarid regions of Argentina; no history of herbicide application, but in the surrounding area, there were patches with 2 and 3 years of annual crops (mainly soybean)	Aparicio et al. 2018
Santa Rosa (La Pampa), Argentina	November 2004 to	Glyphosate: 9.5 µg/kg AMPA: 66.2 µg/kg	Soil analysis conducted in semiarid regions of Argentina in soils with 4 years of annual crops	Aparicio et al. 2018

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	November 2010		(oats, rye, and sorghum) under conventional tillage with little use of pesticides.	
Villa Mercedes (San Luis), Argentina	November 2004 to November 2010	Glyphosate: 131. 5 µg/kg AMPA: 703.5 µg/kg	Soil analysis conducted in semiarid regions of Argentina in soil with 5 years of agricultural activity, mainly annual crops under no tillage and a high use of pesticides.	Aparicio et al. 2018
Mesopotamia Pampas, Argentina	January and March 2012	Glyphosate: 2,299 µg/kg (average) AMPA: 4,204 µg/kg (average)	Samples were collected from 17 agricultural farms. Glyphosate detected in 5/6 samples detected. AMPA detected in 6/6 samples.	Primost et al. 2017

AMPA = aminomethylphosphonic acid; EPA = U.S. Environmental Protection Agency; MDL = method detection limit; STORET = STOrage and RETrieval; USGS = U.S Geological Survey

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A Joint FAO/WHO Meeting on Pesticide Residues summarized glyphosate concentrations found in edible foods following applications of glyphosate formulations representative of several authorized use patterns. Glyphosate concentrations ranged from undetectable, ≤0.05 mg/kg, in several foods like bananas and selected meats to 3.7 mg/kg in a variety of grains and grain-based products (FAO 2005; FAO and WHO 2016). Genetically modified, and conventional food samples were studied. Herbicidal application techniques used on the food samples examined included pre-harvest application, directed ground spray, pre-emergence, and recirculating spray application methods. Application rates ranged from 0.36 to 7.7 kg/ha. The highest concentration found in banana pulp was 0.16 mg/kg. All kiwifruit assessed in the study had undetectable residues. Olives had residues ranging from undetectable to 12 mg/kg. Dry beans had residues ranging from undetectable to 10 mg/kg. Dry peas had residues ranging from undetectable to 8.9 mg/kg. Lentils had residues ranging from undetectable to 17 mg/kg. Glyphosate-tolerant sugar beet root had residues ranging from undetectable to 8.6 mg/kg. Conventional maize had residues ranging from undetectable to 3 mg/kg. Glyphosate-tolerant maize had residues ranging from undetectable to 0.83 mg/kg. Oats had residues ranging from undetectable to 19 mg/kg. Rye grain had residues ranging from 0.1 to 4.6 mg/kg. Wheat grain had residues ranging from 0.09 to 6.4 mg/kg. Sugarcane had residues ranging from undetectable to 15 mg/kg. Coffee and tea had levels ranging from undetectable to 9.6 mg/kg. Glyphosate residues in Kona Hawaiian coffee beans prior to roasting were 0.58 mg/kg, and the roasted beans had residues of 0.06 mg/kg.

Glyphosate was not included in compounds tested for by the Food and Drug Administration's (FDA) Pesticide Residue Monitoring Program (PRMP), nor in the United States Department of Agriculture's Pesticide Data Program (PDP) (FDA 2015; NPIC 2015).

A review by WHO reported that glyphosate was not detected in cereal grains at harvest when application of the herbicide occurred before planting (WHO 2005). Glyphosate was detected in cereals at mean residue levels of 0.2–4.8 mg/kg when application of the herbicide was prior to harvesting. In one assessment, levels of glyphosate were found to decrease upon industrial processing grains to flour from 1.6 to 0.16 mg/kg (WHO 2005). In wheat treated with either Glyfos or Roundup® herbicides, levels of glyphosate were also found to decrease upon processing grains to flour from 0.28–1.0 mg/kg in the grains to <0.05 mg/kg in the flour (FAO 2005). Glyphosate residues in oats stored at room temperature compared to frozen storage were similar, 3.5 and 3.1 mg/kg, respectively (FAO 2005). After exposure to glyphosate at 10 mg/L for 14 days, fish concentrations ranged from 0.2 to 0.7 mg/kg and decreased upon exposure to glyphosate-free water (WHO 2005).

A review by Williams et al. (2000) reported U.S. glyphosate residue data for wheat treated with maximum rates of Roundup®. Wheat crop residues consisted of a mean glyphosate concentration of 0.69 µg/g (mg/kg), with a maximum concentration of 2.95 µg/g (mg/kg). Glyphosate-tolerant soybeans treated with maximum rates of Roundup® showed a mean glyphosate concentration of 2.36 µg/g (mg/kg) and a maximum concentration of 5.47 µg/g (mg/kg).

Glyphosate was detected in carrot samples at average concentrations of 0.078±0.002 mg/kg and in spinach at 0.104±0.005 mg/kg (Zhao et al. 2011).

Glyphosate residues were examined on alder and salmonberry foliage and leaf litter sprayed with glyphosate at 2.0–2.1 kg/ha (Feng et al. 1990b). Foliar residues on alder and salmonberry were 261 and 448 ppm (dry weight), respectively, after the initial application of the herbicide. Leaf litter of alder and salmonberry collected 15 days post-application had glyphosate residues of 12.5 and 19.2 ppm (mg/kg), respectively. After 8–9 days, 50% dissipation was reported for the glyphosate residue. AMPA residues in the leaf litter decreased, and at 29 days after application of the herbicide, concentrations of AMPA were not detected.

5.6   GENERAL POPULATION EXPOSURE

The main routes of exposure to glyphosate for the general public result from the ingestion of foods with residues of glyphosate and foods made from these crops, as well as dermal, ocular, or inhalation exposure from application of herbicides containing glyphosate (EPA 2009c). Glyphosate has been detected in dust samples from homes near glyphosate application sites or from people who brought it indoors on their bodies and/or clothing from glyphosate-treated areas (Curwin et al. 2005). Additionally, pesticide application equipment, such as backpack sprayers, may leak, causing workers to be dermally exposed to glyphosate formulations (NIOSH 2017). Upon dermal exposure, absorption through the skin is expected to be low based on dermal absorption studies, where an estimated 0.8–2.2% percutaneous absorption of glyphosate occurred in a study using ^{14}C-radiolabeled glyphosate in Roundup® (Wester et al. 1991). Evidence has shown that proper hygiene removes glyphosate from skin and will deter absorption through the skin (Wester et al. 1991). Limited monitoring data indicate that oral exposure may occur from drinking contaminated well water supplied from groundwater contaminated with glyphosate; concentrations reported in groundwater are relatively low, and this chemical has low leaching potential from soil to groundwater. Exposure may also occur via ingestion of food with herbicidal residues containing glyphosate as a result of its application. The FDA has not performed a total diet study on

glyphosate. Glyphosate has not been included in the FDAs Pesticide Residue Monitoring Program Reports for the fiscal years 2009 through 2015 (FDA 2013a, 2013b, 2014, 2015, 2016, 2017); however, the FDA in 2016 and 2017 began preliminary testing of samples of soybeans, corn, milk, and eggs for glyphosate residues (FDA 2018). Preliminary results showed no pesticide residue violations for glyphosate in all four commodities tested (soybeans, corn, milk, and eggs). The Joint FAO/WHO Meeting on Pesticide Residues listed International Estimated Daily Intake (IEDI) of glyphosate from 17 GEMS/Food (Global Environment Monitoring System-Food Contamination Monitoring and Assessment Programme) cluster diets to range from 140.5 to 443.0 µg/person (FAO and WHO 2016). Glyphosate is a non-volatile compound, and drift of herbicidal sprays may occur with aerial and ground equipment (Yates et al. 1978); therefore, some exposure via inhalation and direct contact with skin and eyes may occur after members of the general population apply glyphosate during residential use. Although the effects of glyphosate exposure of populations living in areas where glyphosate-containing products have been aerially-applied to eradicate coca crops have been evaluated (Paz-y-Miño et al. 2007, 2011; Solomon et al. 2009), such reports did not include monitoring of exposure levels.

Occupational exposure may occur in both forestry, landscaping, and agricultural settings from the direct use of herbicides containing glyphosate. The most probable routes for occupational exposure are via inhalation and dermal contact with this chemical at workplaces where glyphosate or products containing this chemical are produced or used. Oral exposure may occur from accidental ingestion. During the years 1990–1993, exposure to glyphosate of field workers applying mixtures of Roundup® plus an additional herbicide in areas of Louisiana was assessed (LaDOTD 1995). Mixtures of Roundup® (active ingredient glyphosate) plus Garlon-3A (active ingredient triclopyr) and Roundup® (active ingredient glyphosate) plus 2,4-D (active ingredient 2,4-dichlorophenoxyacetic acid) were applied by 13 workers using spray equipment with operating capabilities of 0.37 L/minute. Glyphosate was detected in the workers' urine using HPLC with a detection limit of 100 ppb. Total excreted urinary amounts of glyphosate ranging from non-detectable to 175 µg/day were reported for both working and non-working days. Urine concentrations were higher than concentrations found in the collected air samples of the breathing zone. It was noted that inhalation exposure was very low compared with threshold limits; the maximum air concentration was 17.9 µg/m^3. Dermal contact and improper hygiene leading to ingestion of the herbicides were noted as the probable routes of exposure.

One-hundred adults older than 50 years who resided in Southern California, as part of the Rancho Bernardo study, were sampled for glyphosate and its metabolite AMPA in 1993-1996 and again in 2014-2016 (Mills et al. 2017). The study did not indicate that any of these adults were involved in application

of pesticides containing glyphosate. In 1993-1996, only 12 participants had glyphosate above the level of detection (LOD=0.03 µg/L) in urine and mean levels were 0.024 for all participants, and 5 participants had detected levels of AMPA (LOD=0.04 µg/L) with the mean levels of 0.008 µg/L for all participants. By 2014-2016 sampling, 70/100 participants had detectable levels of glyphosate and 71/100 of AMPA. Means levels in all 100 participants were 0.314 µg/L and 0.285 µg/L for glyphosate and AMPA, respectively (Mills et al. 2017).

Farmers, with an average age of 45 years licensed as pesticide applicators in South Carolina and Minnesota, who applied herbicides containing glyphosate had average urinary glyphosate levels of 3 µg/L on the day of application (Acquavella et al. 2004). Lack of wearing rubber gloves was associated with higher concentrations in farmers' urine. Spouses, with an average age of 42.2 years residing with the farmers but having minimal or no involvement in the preparation or application of the herbicide, had relatively low and consistent urine concentrations of glyphosate, while children (ages 4–18 years) had an increase followed by a decrease in urine concentrations correlated with application (see Table 5-11). For the entire assessment period, 88–95% of all samples of children's urine were below the detection limit (1 µg/L [ppb] for a 100-mL urine sample). Farmers applying the pesticide had the highest concentrations. The highest concentration of glyphosate found in a child was from a teenage male (29 µg/L [ppb]) who had assisted with mixing and application of the herbicide. An estimated dermal and inhalation exposure value of about 8,000 µg/hour was reported as the highest value from a study of workers employing spray applicators; when corrected for incomplete absorption, this corresponds to an approximate exposure of 50 µg/kg body weight/day (8-hour working day for a 70-kg adult) (IPCS 1994).

Table 5-11. Available Glyphosate Human Monitoring Data

Medium		Concentrations/ minimum, maximum	Average	Notes	Reference
Tissue (brain, blood, liver, kidney)	Postmortem, approximately 12– 13 hours after ingestion	Glyphosate (ppm): kidney 3,650; liver 600; blood; 550; brain; 100		After one individual ingested 200–250 mL Roundup® with 72– 91 g/mL glyphosate	Menkes et al. 1991
Urine	Pre-application	<1–15 µg/L (ppb)	Not reported	Farmers applying pesticide; average age: 45 years	Acquavella et al. 2004
	Day of pesticide application	<1–233 µg/L (ppb)	Geometric mean: 3.2 µg/L (ppb)		
	1-Day post- pesticide application	<1–126 µg/L (ppb)	Geometric Mean: 1.7 µg/L (ppb)		

Table 5-11. Available Glyphosate Human Monitoring Data

Medium	Concentrations/ minimum, maximum	Average	Notes	Reference
2-Day post-pesticide application	<1–81 µg/L (ppb)	Geometric mean: 1.1 µg/L (ppb)		
3-Day post-pesticide application	<1–68 µg/L (ppb)	Geometric mean: 1.0 µg/L (ppb)		
Pre-application	<1–3 µg/L (ppb)	Not reported	Spouses not involved with application; average age: 42 years	
Day of pesticide application	<1–2 µg/L (ppb)	Not reported		
1–3-Day post-pesticide application	<1–1 µg/L (ppb)	Not reported		
Pre-application	<1–17 µg/L (ppb)	Not reported	Children not involved with application; average age: 11.5 years	
Day of pesticide application	<1–29 µg/L (ppb)	Not reported		
1-Day post-pesticide application	<1–24 µg/L (ppb)	Not reported		
2-Day post-pesticide application	<1–12 µg/L (ppb)	Not reported		
3-Day post-pesticide application	<1–6 µg/L (ppb)	Not reported		
Daily during 1-week working period	<0.1 ng/µL		Forest workers using pressurized herbicide sprayers; 8% Roundup® (active ingredient 360 g/L isopropylamine salt)	Jauhiainen et al. 1991
3 Weeks after 1-week working period	<0.1 ng/µL			
General population exposure	Not reported	0.024 µg/L (ppb)	Adults >50 years of age not involved in application in 1993-1996	Mills et al. 2017
General population exposure	Not reported	0.314 µg/L (ppb)	Adults involved in application in 2014-2016; average age: 77.7 years	
Following mild to fatal ingestions of 20–500 mL pesticide	Glyphosate: 228 mg/L mild/moderate case; 22,300 mg/L fatal case; AMPA: 0.54 mg/L mild/moderate case; 91.5 mg/L fatal case		13 individuals ages 25–69 years	Zouaoui et al. 2013
Two occasions (1 month apart) during spring and	0.13–5.4 µg/L	1.4 µg/L	Farm fathers	Curwin et al. 2007b
	0.20–18 µg/L	1.9 µg/L	Non-farm fathers	
	0.062–5.0 µg/L	1.2 µg/L	Farm mothers	
	0.10–11 µg/L	1.5 µg/L	Nonfarm mothers	

Table 5-11. Available Glyphosate Human Monitoring Data

Medium		Concentrations/ minimum, maximum	Average	Notes	Reference
	summer of 2001 (LOD 0.9 µg/L)	0.10–9.4 µg/L	2.7 µg/L	Farm children	
		0.022–18 µg/L	2 µg/L	Non-farm children	
Blood	Following mild to fatal ingestions of 20–500 mL pesticide	Glyphosate: 3.7 mg/L mild/moderate case; 6,640 mg/L fatal case; AMPA: 0.13 mg/L mild/moderate case; 15.4 mg/L fatal case			Zouaoui et al. 2013

AMPA = aminomethylphosphonic acid; LOD = limit of detection

Acquavella et al. (1999) evaluated 1,513 reported cases to the American Association of Poison Control Centers during the years 1993–1997 of ocular or dermal/ocular exposure to Roundup® herbicides with glyphosate concentrations ranging from <2 to >20%. Of all exposure cases, 62% involved male subjects, >80% were in a residential setting, and about 15% were in occupational settings. During the time period, California and Texas had the greatest number of reported cases. Dilute Roundup® formulations accounted for about 82% of the exposures; 5% were with concentrated Roundup®.

Acquavella et al. (2005) analyzed biomonitoring data of farmers before, during and after pesticide application and para-occupational exposure to their spouses and children over a course of five days (1 day before, 1 day during and 3 days post-exposure). Glyphosate was measured in urine at a peak of 3 ppb (LOD 1 ppb) on the day of application and then decreased rapidly. Among the spouse and children of farmers, glyphosate urinary levels remained relatively stable with only appreciable changes in concentration after exposure to pesticide application.

Brouwer et al. (2016) pooled exposure data from three agriculture cohorts from USA, France and Norway, specifically, the Agricultural Health Study (AHS), Agriculture and Cancer Study (AGRICAN) and the Cancer in the Norwegian Agricultural Population (CNAP), respectively. Among 316,270 participants who were pesticide applicators or farmers (active or retired), 99% reported ever using any pesticide of which 44% reported to have ever been exposed to glyphosate, ranging between 1 to 21 years of exposure. Specifically, 129,327 men (54%) and 41,276 (14%) females were exposed to glyphosate across the three cohorts.

Aris and LeBlanc (2011) examined blood concentrations of glyphosate in a group of 30 pregnant and 39 non-pregnant females residing in Sherbrooke, Canada. The study noted that none of the subjects

worked or lived with an individual who worked with pesticides. Neither glyphosate nor AMPA were
detected in the maternal or fetal cord serum of pregnant subjects. Additionally, AMPA was not detected
in non-pregnant subjects. Glyphosate was detected in 5% of the non-pregnant subjects at a range of not
detectable to 93.6 ng/mL, with a mean of 73.6 ng/mL (LOD=15 ng/mL).

The Fourth National Report on Human Exposures to Environmental Chemicals, published and updated by
the Centers for Disease Control and Prevention reporting biomonitoring data from the National Health
and Nutrition Examination Survey (NHANES), does not include data for glyphosate or its metabolite,
AMPA (CDC 2019).

As with the adult general population, exposure of children to glyphosate may occur through ingestion of
foods with residues of glyphosate and foods made from these crops, as well as inhalation, dermal contact,
and/or ocular contact when in the proximity of areas where glyphosate containing herbicides have been
recently applied. Glyphosate has been detected in dust samples from homes near glyphosate application
sites or from people who brought it indoors on their bodies and/or clothing from glyphosate-treated areas
(Curwin et al. 2005). Limited monitoring data indicate that oral exposure may occur from drinking
contaminated well water supplied from groundwater contaminated with glyphosate; concentrations
reported in groundwater are relatively low, and this chemical has low leaching potential from soil to
groundwater. It is unclear if breastmilk is a route of exposure for glyphosate as there are only two studies
which have evaluated this route (Bus 2015 and McGuire et al., 2016). According to Bus (2015)
glyphosate is not likely to bioaccumulate in breast milk and McGuire et al., 2016 did not detect it in
breast milk from lactating mothers with detectable glyphosate in their urine (McGuire et al. 2016).

During the spring and summer of 2001, urinary pesticide concentrations were investigated in families
residing in non-farm and farm households located in Iowa (Curwin et al. 2007a, 2007b). Urinary
glyphosate levels were fairly similar between farm and non-farm households. In addition, glyphosate
concentrations were fairly similar when comparing individuals living on farms where the pesticide was
used with those living on farms where the pesticide was not used. Glyphosate was detected at urinary
levels equal to or greater than the LOD (0.9 µg/L) in 66% of the 23 non-farm fathers, 75% of the 24 farm
fathers, 65% of the 24 non-farm mothers, 67% of the farm mothers, 88% of the non-farm children, and
81% of the farm children (Curwin et al. 2007b). Estimated glyphosate intakes among 40 children
(17 homes) living on farms where glyphosate was applied ranged from 0.001 to 0.33 µg/kg/day, with 16%
of the samples below the LOD (Curwin et al. 2007a). Estimated glyphosate intakes among 25 children

(8 homes) living on farms where glyphosate was not applied ranged from 0.003 to 0.64 µg/kg/day, with 20% of the samples below the LOD.

McQueen et al. (2012) estimated the mean glyphosate dietary exposure of 43 pregnant women at 0.001 mg/kg body weight/day and these exposures were well below applicable health guidelines. Since only a small percentage of glyphosate crosses the placenta, fetal exposure resulting from maternal exposure to glyphosate was minimal.

5.7   POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Farm workers, farming families, landscaping workers, and people of all ages living and or working in agricultural sectors will incur higher exposure to glyphosate, as agriculture is the largest industry for herbicide use. Field workers who apply herbicides containing glyphosate will likely incur higher exposures to this chemical. Levels of glyphosate in field workers' urine has been shown to increase during spraying season; however, glyphosate levels did not appear to carry over from previous seasons (LaDOTD 1995).