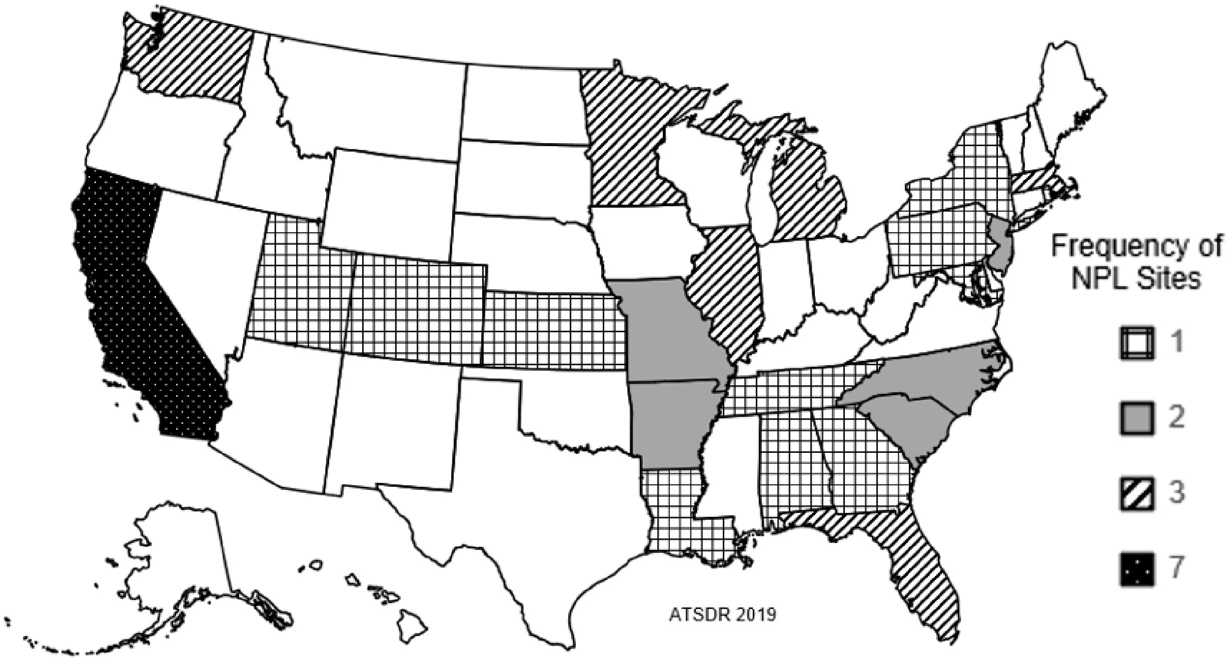
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

2,4-D has been identified in at least 46 of the 1,867 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2019). However, the number of sites in which 2,4-D has been evaluated is not known. The number of sites in each state is shown in Figure 5-1.

Figure 5-1. Number of NPL Sites with 2,4-D Contamination



- People can be exposed to 2,4-D through:
  - Inhalation of contaminated air
  - Consumption of food sources that contain 2,4-D residue
  - Dermal contact with 2,4-D during its application or by entering an area where it was very recently applied

- Environmental exposure of 2,4-D can occur:
  - During manufacturing processes 2,4-D
  - During or following application of 2,4-D to control weeds

- In the environment, 2,4-D is expected to:
  - Oxidize in the atmosphere or be removed by wet or dry deposition
  - Undergo photolysis in sunlit water and metabolism by aerobic bacteria
  - Readily undergo biodegradation and photodegradation from soil

2,4-D is one of the most widely used agricultural herbicides in the United States, with approximately 38 million pounds applied to crops in 2014, with pasture and hay fields, wheat, soybeans, and corn crops receiving the greatest applications (USGS 2016). It is also applied to residential or commercial turf for the elimination of a wide variety of broadleaf weeds without causing harm to the grass. Direct applications to rivers or lakes are occasionally made to control certain aquatic plants such as water chestnut or milfoil. Most forms of 2,4-D that are used today are supplied as the dimethyl amine salt (2,4-D DMA) or the ethylhexyl ester (2,4-D EHE).

In the atmosphere, 2,4-D is expected to exist in both the vapor and particulate phase. Vapor-phase 2,4-D is degraded by reaction with photochemically generated hydroxyl radicals with an estimated half-life of about 19 hours (Meylan and Howard 1993). Particulate-phase 2,4,-D is removed from the atmosphere by wet and dry deposition. Atmospheric levels of 2,4-D are generally very low, but detectable levels may be present in agricultural areas where 2,4-D has been applied as an herbicide (WHO 2003).

2,4-D may enter rivers, lakes, and ponds from spray drift following its aerial application or from runoff and erosion of soils treated with 2,4-D. It may also be directly applied to water surfaces in order to eradicate nuisance aquatic plants (Eyres 2009). The aerobic aquatic metabolism half-life of 2,4-D was reported to be about 15 days; however, it was more persistent in anaerobic aquatic metabolism studies, with a half-life ranging from about 41 to 333 days (EPA 2005a). Photolysis in sunlit surface waters may also be an important environmental fate process for 2,4-D, but hydrolysis under environmental conditions is expected to be negligible. Volatilization from water surfaces is not expected to be an important environmental fate process since 2,4-D salts do not volatilize. A bioconcentration factor (BCF) of 1, measured in carp, suggests that bioconcentration in aquatic species is expected to be low (NITE 2010a).

Field dissipation studies conducted in seven states over a 2-year period suggest that 2,4-D is not highly persistent in soils, with half-lives typically ranging from a few days to a few weeks depending upon the soil properties, water content of the soil, and whether 2,4-D was applied as a liquid or granular formulation (Wilson et al. 1997). The EPA reported that the biodegradation half-life of 2,4-D in an aerobic mineral soil was 6.2 days and the photodegradation half-life in soil was 68 days (EPA 2005a). Organic carbon normalized soil adsorption coefficients (K_{oc}) values of 70, 76, 59, and 117 using a sandy loam, sand, silty clay loam, and loam soil, respectively, suggest that adsorption to soil surfaces is low (EPA 2005a). Even though 2,4-D is expected to have high mobility in soils, its ability to leach into groundwater may be attenuated by its relatively short half-life in soils.

The general population is exposed to 2,4-D through both its agricultural and residential use. Ingestion of food and water contaminated with small residues of 2,4-D may occur for the general population. Persons residing within or very near areas of heavy 2,4-D use (e.g., farms) would have had an increased risk of exposure to greater amounts of 2,4-D through dermal contact with contaminated plants, soils, or surface waters or by inhalation from the applied herbicide. Those likely to receive the highest exposures are those who are involved in the production, formulation, handling, and application of 2,4-D. Dermal contact appears to be the major route of exposure for workers, although inhalation exposure and accidental ingestion via hand-to-mouth activity is possible. 2,4-D was detected in indoor air and on surfaces (floors, tabletops, and windowsills) inside single-story Midwestern residences following lawn applications (Nishioka et al. 2001). It was determined that the main transport routes of 2,4-D into the home were from the homeowner applicator and by pets.

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

2,4-D is an herbicide belonging to the phenoxyacetic acid chemical family (NPIC 2008). It is produced by the reaction of 2,4-dichlorophenolate with monochloroacetic acid or by the reaction between 2,4-dichlorophenol and chloroacetic acid in aqueous sodium hydroxide (HSDB 2015). 2,4-D is sold commercially in the following formulations: emulsifiable concentrate, wettable granules, wettable powder, emulsion (esters), and aqueous solution (salts) (Meister et al. 2014).

Annual production of 2,4-D in the United States was estimated to be 52–67 and 47 million pounds in 1990 and 2001, respectively. Production in the United States was said to be between 50 and <100 million pounds in 2006 according to the EPA’s Inventory Update Rule (IUR) (HSDB 2015). The EPA has replaced the IUR with the Chemical Data Reporting (CDR) Rule, which requires manufacturers (including importers) to give EPA nonconfidential information on the chemicals that they manufacture domestically or import into the United States. Data from the CDR lists only one producer of 2,4-D in the United States (the Dow Chemical Company), which declared their production volume as confidential business information for 2012 (EPA 2015a).

2,4-D is a chemical that manufacturing and processing facilities would be required to report under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986 [SARA]) (EPA 2005b). Table 5-1 lists the production year, number of facilities, the state where each facility is located, and the range (in pounds) for each domestic manufacturer that reported production or formulation of 2,4-D in 2014 (TRI13 2015). Manufacturers are required to report Toxics Release Inventory (TRI) data to satisfy EPA requirements. The TRI data should be used with caution since only certain types of facilities are required to report (EPA 2005b). This is not an exhaustive list.

Table 5-1. Facilities that Produce, Process, or Use 2,4-D

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AR	1	100,000	999,999	9, 12
CA	1	10,000	99,999	7, 9
GA	1	1,000,000	9,999,999	7, 9
IA	2	100,000	9,999,999	7
IL	3	1,000	999,999	1, 2, 3, 4, 6, 7, 12
IN	1	Not available	Not available	Not available
KS	2	1,000,000	9,999,999	2, 3, 6, 7
MI	3	0	9,999,999	1, 3, 4, 6, 9, 12
MO	1	1,000,000	9,999,999	2, 3, 4, 6, 7
MS	1	100,000	999,999	7
MT	1	1,000,000	9,999,999	6, 7
NE	1	1,000	9,999	12
OH	4	100	999,999	7, 12
PA	1	Not available	Not available	Not available
TN	1	1,000,000	9,999,999	6, 7, 8, 9
TX	2	1,000	999,999	12
UT	1	100,000	999,999	9, 12
WI	1	Not available	Not available	Not available

[a] Post office state abbreviations used.
[b] Amounts on site reported by facilities in each state.
[c] Activities/Uses:

1. Produce
2. Import
3. Used Processing
4. Sale/Distribution
5. Byproduct
6. Reactant
7. Formulation Component
8. Article Component
9. Repackaging
10. Chemical Processing Aid
11. Manufacture Aid
12. Ancillary
13. Manufacture Impurity
14. Process Impurity

Source: TRI16 2018 (Data are from 2016)

5.2.2 Import/Export

No current information regarding the import or export of 2,4-D could be located.

5.2.3 Use

While the free acid is itself used as an herbicide, there are nine forms of 2,4-D registered as active ingredients in end use products. These include salts, amines, and esters of 2,4-D (EPA 2005a). Derivatives include the sodium salt, diethanolamine salt, dimethyl amine salt, isopropylamine salt, triisopropanolamine salt, butoxyethyl ester, ethylhexyl ester, and isopropyl ester. Almost 90–95% of total 2,4-D global use is accounted for by the dimethyl amine salt and ethylhexyl ester (NPIC 2008). 2,4-D and its different chemical forms are listed as an ingredient, either as the singular active ingredient or in conjunction with other ingredients, in about 600 agricultural and residential products (EPA 2005a). The use of 2,4-D ranks first among herbicides in frequency of home and garden applications and third in national herbicide use for agriculture (Gilliom et al. 1999).

2,4-D is sometimes confused with the similarly named chemical, 2,4,5-T, which at one point in time was contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin, or TCDD, a confirmed toxin (CDC 2013). However, TCDD has never been a known contaminant of 2,4-D.

2,4-D is used on a wide range of broadleaf and aquatic weeds (EPA 2005a). Registered uses for 2,4-D can be seen in Table 5-2. These uses include application on field, fruit, and vegetable crops, as well as eliminating broadleaf weeds in turf, commercial and residential lawns while not harming the grass, and aquatic and forestry applications. The Midwest, Great Plains, and Northwestern United States have the most 2,4-D usage (EPA 2005a).

Table 5-2. Registered Uses for 2,4-D

Crop grouping	Representative crops
Terrestrial food crop	Pear, pistachio, stone fruits
Terrestrial food and feed crop	Agricultural fallow/idleland; agricultural rights-of-way/fencerows/ hedgerows; agricultural uncultivated areas; apple; barley; citrus fruits; corn (unspecified); corn, field; corn, pop; corn, sweet; fruits (unspecified); grapefruit; lemon; oats; orange; pome fruits; rice; rye; small fruits; soil, preplant/outdoor; sorghum (unspecified); soybeans (unspecified); sugarcane; tangelo; tree nuts; wheat
Terrestrial feed crop	Grass forage/fodder/hay; pastures; rangeland; rye; sorghum

Table 5-2. Registered Uses for 2,4-D

Crop grouping	Representative crops
Terrestrial nonfood crop	Agricultural fallow/idleland; agricultural rights-of-way/fencerows/hedgerows; agricultural uncultivated areas; airports/landing fields; Christmas tree plantations; commercial/industrial lawns; commercial/institutional/industrial, premises/equipment (outdoor); forest nursery plantings (for transplant purposes); golf course turf; grasses grown for seed; industrial areas (outdoor); nonagricultural outdoor buildings/structures; nonagricultural rights-of-way/fencerows/hedgerows; nonagricultural uncultivated areas/soils; ornamental and/or shade trees; ornamental lawns and turf; ornamental sod farm (turf); ornamental woody shrubs and vines; paved areas (private roads/sidewalks); potting soil/topsoil; recreation area lawns; recreational area; soil, preplant/outdoor; urban areas
Terrestrial nonfood and outdoor residential	Fencerows/hedgerows; nonagricultural rights-of-way/fencerows/hedgerows; ornamental and/or shade trees; ornamental lawns and turf; ornamental woody shrubs and vines; paths/patios; paved areas (private roads/sidewalks); urban areas
Aquatic food crop	Agricultural drainage systems; aquatic areas/water; commercial fishery water systems; irrigation systems; lakes/ponds/reservoirs (with human or wildlife use); rice; streams/rivers/channeled water; swamps/marshes/wetlands/stagnant water
Aquatic nonfood outdoor	Aquatic areas/water; streams/rivers/channeled water; swamps/marshes/wetlands/stagnant water
Aquatic nonfood industrial	Drainage systems; industrial waste disposal systems; lakes/ponds/reservoirs (without human or wildlife use)
Forestry	Conifer release; forest plantings (reforestation programs) (tree farms, tree plantations, etc.); forest tree management/forest pest management; forest trees (all or unspecified); forest trees (hardwoods, broadleaf trees); pine (forest/shelterbelt)
Outdoor residential	Residential lawns
Indoor nonfood	Commercial transportation facilities-nonfeed/nonfood

Source: EPA 2005a

2,4-D has been used in the United States since the 1940s (EPA 2005a). Due to some human health concerns, 2,4-D was placed in pre-Special Review by the EPA in 1986. In 1988, it was proposed that Special Review not be initiated due to the lack of epidemiological data linking 2,4-D and carcinogenicity and the final decision was deferred until reregistration. Between 1988 and evaluation for reregistration in 2005, the EPA performed several reviews of epidemiological and other data and still found that none of the new data definitively linked 2,4-D to human cancer cases. In order to address future concerns about its safety, the 2,4-D Industry Task Force agreed to certain changes to labeled uses to reduce exposure. In 2005, the EPA drafted its Reregistration Eligibility Decision (RED) and it was determined that 2,4-D was eligible for reregistration and the final notice not to initiate Special Review was issued (EPA 2005a).

The total annual use of 2,4-D in the United States was approximately 46 million pounds, based on data collected from 1992 through 2000. Agricultural use accounted for 66%, or 30 million pounds, while non-agricultural use accounted for 34%, or 16 million pounds. Broken down into area of use in terms of pounds, total 2,4-D use was distributed in the following pattern: pasture and rangeland, 24%; residential lawn with fertilizer, 12%; spring wheat, 8%; winter wheat, 7%; lawn and garden by lawn care and landscape professionals, 7%; residential lawn without fertilizer, 6%; field corn, 6%; soybeans, 4%, summer fallow, 3%; hay not including alfalfa, 3%, and roadways, 3% (EPA 2005a). Use varies from year to year. The U.S. Geological Survey (USGS) Pesticide National Synthesis Project estimated that approximately 38 million pounds of 2,4-D was applied to crops in 2014, with pasture and hay fields, wheat, soybeans, and corn crops receiving the greatest applications (USGS 2016). The development of genetically modified crops that have an increased tolerance to 2,4-D may cause an increase in the total amount applied annually to crops such as soybeans (EPA 2016a). Recently, the EPA granted the registration of a new herbicide named Enlist Duo™ containing 2,4-D choline salt and glyphosate for use on genetically modified corn, soybean, and cotton crops designed to be resistant to 2,4-D and glyphosate (EPA 2017).

5.2.4 Disposal

2,4-D should be disposed of by means in accordance with local regulations, such as incineration (Meister et al. 2014).

2,4-D is known to be degraded by soil microorganisms, and therefore, burial in non-crop areas away from water supplies may be an acceptable method of disposal for small quantities (HSDB 2015). The most environmentally acceptable means for 2,4-D disposal is by incineration. Triple rinsing and draining are used for the decontamination of 2,4-D containers and drums. Chemical treatment involves detoxification with chloride of lime or sodium carbonate. Removal of 2,4-D from water may be achieved through the use of activated charcoal or by coagulation and complete treatment by ozonation (HSDB 2015).

5.3 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (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).

5.3.1 Air

Estimated releases of 1,163 pounds (~0.53 metric tons) of 2,4-D to the atmosphere from 27 domestic manufacturing and processing facilities in 2016, accounted for about 0.34% of the estimated total environmental releases from facilities required to report to the TRI (TRI16 2018). These releases are summarized in Table 5-3.

2,4-D is released to the air during application with a wide range of equipment including fixed-wing aircraft, backpack sprayer, band sprayer, boom sprayer, ground directed sprayer, handheld sprayer, helicopter, and tractor-mounted sprayer as well as airblast and chemigation application (EPA 2005a). Available information on the releases of 2,4-D to the air in occupational settings and indoor air, along with exposure levels, is provided in Section 5.6.

Table 5-3. Releases to the Environment from Facilities that Produce, Process, or Use 2,4-D[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AR	1	1	0	0	0	0	1	No data	1
CA	1	2	0	0	15	0	2	15	17
GA	1	0	0	0	0	481	0	481	481
IA	2	481	0	0	0	0	481	No data	481
IL	3	14	0	0	1,073	0	14	1,073	1,087

Table 5-3. Releases to the Environment from Facilities that Produce, Process, or Use 2,4-D[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
IN	1	0	No data	0	0	0	No data	No data	No data
KS	2	10	0	0	188	0	10	188	198
MI	2	144	17	0	277,711	0	277,872	0	277,872
MO	1	204	0	0	669	0	204	669	873
MS	1	0	0	0	0	0	0	No data	0
MT	1	10	0	0	0	0	10	No data	10
NE	1	10	0	0	750	0	10	750	760
OH	4	256	0	56,898	13	135	57,154	148	57,302
PA	1	0	No data	0	0	0	No data	No data	No data
TN	1	2	0	0	0	0	2	No data	2
TX	2	28	0	0	0	0	28	No data	28
UT	1	2	0	0	0	0	2	No data	2
WI	1	0	No data	0	0	0	No data	No data	No data
Total	27	1,163	17	56,898	280,419	616	335,789	3,324	339,113

[a] The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b] Data in TRI are maximum amounts released by each facility.
[c] Post office state abbreviations are used.
[d] Number of reporting facilities.
[e] The sum of fugitive and point source releases are included in releases to air by a given facility.
[f] Surface water discharges, wastewater treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g] Class I wells, Class II-V wells, and underground injection.
[h] Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i] Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown
[j] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k] Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI16 2018 (Data are from 2016)

5.3.2 Water

Estimated releases of 17 pounds (~0.01 metric tons) of 2,4-D to surface water from 27 domestic manufacturing and processing facilities in 2016, accounted for <0.01% of the estimated total environmental releases from facilities required to report to the TRI (TRI16 2018). This estimate includes releases to wastewater treatment and publicly owned treatment works (POTWs). These releases are summarized in Table 5-3.

2,4-D may enter the aquatic environment through direct application to water for weed control, disposal of wastes from manufacturing and production plants, runoff from treated lands, and drift from application (Sikka et al. 1976).

In 1969, a monitoring program of the irrigation water in the Columbia Basin in Washington reported that the 2,4-D application rate on canal bank weeds ranged from 1.4 to 2.5 pounds per acre (lbs/A) (1.57–2.8 kg/hectare) for a distance of up to 5.1 miles (Bartley and Hattrup 1970). During April–June 1969, about 170,000 gallons of 2,4-D (dimethyl amine salt) was applied to over 18,000 surface acres of Nickajack and Guntersville Reservoirs in Tennessee (Wojtalik et al. 1971). 2,4-D is used to treat aquatic waterbodies for the invasive European water chestnut (*Trapa natans L.)* and Eurasian water milfoil; this likely accounts for most of the intentional releases of this substance to surface waters. For example, in the summers of 2006, 2007, and 2008, 2,4-D was applied at a rate of 150, 200, and 200 lbs/A, respectively, to a 40-acre wetland in Oneonta, New York in close proximity to the Susquehanna River in order to eradicate overgrowth of water chestnut in this water body (Eyres 2009). 2,4-D formulations (Navigate®, Aquacide® and AquaKleen®) were also applied to a lake in East Haddam, Connecticut between 1999 and 2001 to control milfoil (Bugbee et al. 2003). Most states have strict use guidelines on using 2,4-D in aquatic environments and may require the use of a permit from the state's department of environmental conservation in order to apply these formulations to water bodies. The maximum 2,4-D (acid equivalent) rate for aquatic uses on submerged aquatic plants set by the EPA is 10.8 pounds/acre foot (EPA 2005a).

Effluent samples collected from 52 of the largest municipal wastewater treatment plants and water pollution control facilities in Oregon contained 2,4-D in 3 of 102 samples at a median concentration of 1,630 ng/L and a maximum concentration of 1,890 ng/L in 2010 (Hope et al. 2012).

5.3.3 Soil

Estimated releases of 280,419 pounds (~127.19 metric tons) of 2,4-D to soil from 27 domestic manufacturing and processing facilities in 2016, accounted for about 82.69% of the estimated total environmental releases from facilities required to report to the TRI (TRI16 2018). An additional

56,898 pounds (~25.81 metric tons), constituting about 16.78% of the total environmental emissions, were released via underground injection (TRI16 2018). These releases are summarized in Table 5-3.

More than 3.8 million kg (8.4 million pounds) of 2,4-D were applied to cereal crops in the three prairie provinces (Alberta, Saskatchewan, and Manitoba) of Canada in 1990 (Waite et al. 2002).

The rate per application and rate per year for 2,4-D (acid equivalent) are typically <1.5 and 2.0 pounds/acre/year, respectively (EPA 2005a). The maximum rate for asparagus, forestry uses, and non-cropland uses is 4.0 pounds/acre/year.

Because of its rapid biodegradation in soil, 2,4-D is not likely to be found in soil, except possibly near point sources after immediate release.

5.4 ENVIRONMENTAL FATE

The dominant process affecting the overall environmental fate of 2,4-D is degradation by microbiological activity (Wilson et al. 1997).

5.4.1 Transport and Partitioning

Air. Based on the vapor pressure of 2,4-D (see Table 4-3), 2,4-D released to the atmosphere via spraying applications would be expected to exist in both the vapor and particulate phases (Bidleman 1988).

Water. 2,4-D is released to water both from direct application for weed control, and through unintentional processes such as spray drift and runoff. Volatilization is not expected to be significant from water since most formulations of 2,4-D are as salts, which do not volatilize. 2,4-D released to water is not expected to be adsorbed to soils and sediments based on its organic carbon partition coefficient (Koc) values (EPA 1980, 2005; Rao and Davidson 1982; USDA 2001).

Sediment and Soil. 2,4-D released to soil partitions to surface water via runoff and to groundwater as a result of leaching. Volatilization of 2,4-D from moist and dry soils is not expected to be a significant transport process. 2,4-D ethylhexyl ester (2,4-D EHE) applied to a sandy loam at a rate of 15.8 lbs/acre was not volatile (<0.22% of the initial amount volatilized) over the course of a 30-day experiment (EPA

2004). It was observed that 2,4-D EHE rapidly transformed to 2,4-D (half-life 8 days), which is expected to exist as an anion under environmental conditions, and anions do not volatilize.

The mobility of 2,4-D in soils and sediments is expected to be high based on measured organic carbon corrected soil adsorption coefficient (K_{oc}) values. An average K_{oc} value of 19.6 was reported in nine soils tested (Rao and Davidson 1982). EPA (1980) measured an average K_{oc} of 109.1 in three soils (a silty clay loam, a sandy clay loam, and fine sand) with a range of 72.2–135.7. This study also reported that as the concentration of 2,4-D in the soil solution phase increased, the mobility increased. The ARS Pesticide Property Database lists Koc values for 2,4-D ranging from 20 to 79 (USDA 2001). Koc values of 70, 76, 59, and 117 were measured using a sandy loam, sand, silty clay loam, and loam soil, respectively (EPA 2005a). Despite the relatively low soil adsorption coefficients of 2,4-D, field dissipation studies have typically indicated only moderate leaching to lower soil levels due to the relatively rapid rate of degradation of 2,4-D (EPA 2004, 2005; Wilson et al. 1997).

2,4-D usually exists as an anion in the environment based its pKa of 2.73 (USDA 2001). Anionic compounds generally adsorb less than their neutral forms to clay or soils with organic carbon (Doucette 2000). Vasudevan and Cooper (2004) showed that soil mineralogy (iron and aluminum oxide content) and exchangeable aluminum content had a direct relationship with the adsorption of anionic 2,4-D, while soil phosphate content had an inverse effect, suggesting that 2,4-D will be more easily leached in soils subject to continued phosphate fertilization and liming. Soil pH also has an effect on mobility. In a study of four soils from rice-producing areas of Arkansas at pH 5 and 7, the mean adsorption coefficient (Kd) of 2,4-D ranged from 0.06 to 0.59 L/kg, and demonstrated that sorption was greatest and mobility was lowest at lower pH, as more of the substance would exist as the fully protonated acid rather than the conjugate base (Johnson et al. 1995).

Other Media. Bioaccumulation in aquatic organisms is not expected to be significant, based on a measured bioconcentration factor (BCF) of one for carp (Cyprinus carpio) exposed to 1 mg/L of 2,4-D for 28 days (NITE 2010a). Daphnid (Daphnia magna, a sand flea) and channel catfish (Ictalurus melas) exposed to 0.01 ppm 2,4-D over a period of 4 days had measured depuration half-lives of 13.8 hours and 1.32 days, respectively (Ellgehausen et al. 1980). Rodgers and Stalling (1972) performed a study in which fed and fasted bluegills and channel catfish were exposed to 1.0 mg/L of 14C-labeled 2,4-D butoxyethanol ester for up to 120 hours. Fed channel catfish and bluegills contained 7.3 and 7.8 μg/g (whole body) of 2,4-D after 1 hour of exposure. These levels decreased to 0.04 and 0.45 μg/g, respectively, after 24 hours of exposure, suggesting that uptake and elimination are rapid, but the rates are different for the two species of fish. Similar trends were observed in the fasted fish. Whole-body levels of 9.03 and 16.67 μg/g of 2,4-D after 1 hour of exposure were observed for catfish and bluegills, respectively. These levels increased to 15.74 and 54.55 μg/g, respectively, after 6 hours and then declined to 1.20 and 7.50 μg/g, respectively, after 24 hours, indicating differential uptake and elimination rates between the species of fish. The slower elimination rate of 2,4-D in bluegills versus the channel catfish was further evidenced by the examination of 2,4-D residues in certain organisms of the fish. For example, blood samples of bluegills contained 20.9 μg/g after 8 hours of exposure, whereas catfish contained only 0.1 μg/g; liver samples of catfish contained 0.5 μg/g, while liver samples of bluegills contained 37.6 μg/g after 8 hours.

Bioaccumulation factors of 6 and <10 were reported for exposure to 50 μg/L 2,4-D in algae after 24 hours in a static system and in golden orfe (a fish) after 3 days, respectively (Freitag et al. 1982). Three seaweed species, Ulva sp., Enteromorpha sp., and Rhodymenia sp., exposed to 25 ppb of 2,4-D had a measured uptake of 0.01–0.03% after 24 hours of exposure (Sikka et al. 1976).

5.4.2 Transformation and Degradation

Degradation of 2,4-D is primarily by microbiological activity (Wilson et al. 1997). 2,4-D has been shown to undergo degradation in pure cultures by particular species of aerobic microorganisms. The two main pathways of degradation break apart bonds and transform the molecule, creating a hydroxyphenoxy acetic acid intermediate or by acting upon the corresponding phenol (WHO 1989). Half-lives for 2,4-D range from 1.8 to 3.1 days via degradation with a mixture of activated sludge, soil, and sediment microorganisms (Liu et al. 1981).

Air. A structure estimation method (Meylan and Howard 1993) was used to approximate a 19-hour half-life for the reaction of 2,4-D with hydroxyl radicals based on a vapor phase reaction rate constant of 6.6×10^{-12} cm^3/molecule-second at 25°C. 2,4-D may be susceptible to photolysis by direct sunlight, based on an ultraviolet maxima in the 280–290 range for phenoxy herbicides in aqueous media (HSDB 2015).

Water. 2,4-D, present at 100 mg/L, reached 0% of its theoretical biological oxygen demand (BOD) in 4 weeks using an activated sludge inoculum at 30 mg/L in the Japanese Ministry of International Trade and Industry (MITI) test (NITE 2010b). However, in other studies, 2,4-D was shown to degrade significantly in sewage sludge. More than 90% of 2,4-D at a concentration of 10–100 ng was mineralized in sewage after 28 days (Subba-Rao et al. 1982). Rosenberg and Alexander (1980) reported that nearly all 2,4-D applied to municipal sewage was degraded after 7 days, and that further additions of 2,4-D were degraded without a lag period.

Radiolabeled 2,4-D at an initial concentration of 4.63 µg/g had a first-order degradation half-life of 15 days using a sediment and water mesocosm maintained under aerobic conditions (EPA 2004). Soluble degradation products identified in the study were chlorohydroquinone and 2,4-dichlorophenol (DCP).

Nesbitt and Watson (1980) showed that the rate of degradation of 2,4-D in river water was directly related to the sediment load and the nutrient concentration; however, the addition of organisms capable of degradation had no effect. 2,4-D incubated in sediment and unfiltered river water obtained during flood conditions degraded quickly with and without the addition of nutrients, which suggests that the water already possessed high phosphorous and nitrogen levels capable of sustaining microbial populations that degrade 2,4-D. This study reported ranges of half-lives of 2,4-D in river water from 18 to >50 days for clear water with low nutrient loadings and from 10 to 25 days for muddy (nutrient and sediment rich) water obtained after heavy rainfall and flooding conditions with lag times of 6–12 days.

In natural lake water, the extent of mineralization of 2,4-D was reported as 72% in 50 days and was shown to be enhanced by levels of both organics (62.7–95.8% mineralization) and inorganics (84% mineralization) in the water (Wang et al. 1984). Mineralization was also shown to be more rapid at higher concentrations of 2,4-D. This was demonstrated in another study that reported 75–90% mineralization of 2,4-D at concentrations of ≤500 pg/mL in eutrophic lake water in 28 days, but 34% was mineralized at a concentration of 4.9 ng/mL (Subba-Rao et al. 1982).

Preconditioning of organisms to 2,4-D may also increase the rate of degradation. This was shown in a study of the biodegradation of 2,4-D in river water during seasonal variation, which indicated that during different seasons, there was an effect on both 2,4-D concentrations in the water and its degrading capacity (Watson 1977). In these experiments, river water and mud were collected throughout the year from rivers draining from an agricultural region with 2,4-D use and compared to samples collected from rivers draining from forest regions with no recorded 2,4-D use or fertilizer applications. Greater degradation of 2,4-D was observed in the river waters and muds from the agricultural region as compared to the forest region. This was most notable using samples collected after heavy rainfall and flooding conditions where nutrient loadings from fertilizer usage in the agricultural location was common in the runoff into the river. In addition, the soils and waters surrounding the agricultural area with a history of 2,4-D usage is likely to contain greater colonies of microorganisms acclimated to degrading 2,4-D and other herbicides as compared to soils and water from the forest region with no history of herbicide usage. Other factors such as, but not limited to, nutrient load, amount of 2,4-D degrading bacteria, and rainfall amounts are also instrumental in how quickly and how much 2,4-D can be degraded.

2,4-D is stable to hydrolysis (EPA 2005a). In sodium phosphate-buffered waters at pH 2, 7, and 10, there was no observed hydrolysis of 2,4-D, present at 25 μg/L (Chamberlain et al. 2012). Radiolabeled 2,4-D EHE at an initial concentration of 30 μg/L had a first-order half-life of 99.7 days in pH 5 buffer solution, 48.3 days in pH 7 buffer solution, and 52.2 hours in pH 9 buffer solution (EPA 2004).

2,4-D may undergo some degree of photodegradation in surface waters. In a water solution irradiated at 356 nm, 2,4-D had reported photolysis half-lives of 2–4 days (Baur and Bovey 1974). 2,4-D had a half-life of 50 minutes in water irradiated at 254 nm with reaction products 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1,2,4-benzenetriol, and polymeric humic acids (Crosby and Tutass 1966). Furman et al. (2013) studied the photolysis rate of 2,4-D and atrazine in surface water samples collected from agricultural areas in four drainages of the Columbia River Basin in Washington State. They attempted to correlate the photolysis rates with three water quality parameters: nitrate levels in the surface water, dissolved organic carbon levels, and amount of suspended solids in the water samples. An average photolysis rate constant of 0.039/hour was reported for 2,4-D in surface water samples irradiated using a xenon arc lamp, which corresponds to a photolysis half-life of about 18 hours (Furman et al. 2013). Photolysis rates were increased in waters with high nitrate levels as the irradiation of nitrate in surface waters results in the production of hydroxyl radicals, which oxidize 2,4-D and other organic substances. Levels of dissolved organic carbon also showed a positive correlation with the photolysis rate of 2,4-D; however, the levels of suspended solids were inversely proportional to the photolysis rate in the surface water samples at one location. Radiolabeled 2,4-D EHE had a first-order half-life of 128.2 days in pH 5 buffer solution when irradiated with natural sunlight, while a dark control had a half-life of 252.5 days in the pH 5 buffer (EPA 2004). The main photodegradation products were 2,4-D and 2,4-DCP (Furman et al. 2013).

Sediment and Soil. 2,4-D undergoes biodegradation in soils under most conditions and is not considered persistent. The rate of degradation is affected by nutrient levels, oxygen levels, moisture, temperature, presence of microorganisms, concentration of 2,4-D and whether the soils had previously been acclimated with 2,4-D or other similar herbicides (WHO 1989). Under differing conditions, typical reported half-lives of 2,4-D ranged from <1 day to several weeks (Eder and Weber 1980; Foster and McKercher 1973; Liu et al. 1981; Ou 1984; Rao and Davidson 1982). The EPA Registration Eligibility

Decision document for 2,4-D reported that its half-life in an aerobic mineral soil was 6.2 days with several noted metabolites, including 1,2,4-benzenetriol, 2,4-DCP, 2,4-dichloroanisole (DCA), and 4-chlorophenol (EPA 2005a).

Increased moisture, temperature, and organic matter stimulate the degradation of 2,4-D, as demonstrated in a study of the herbicide in two soil types under dry and moist conditions and at two different temperatures (Ou 1984). 2,4,-D was rapidly mineralized using surface soil samples (0–15 cm depth) of a Cecil loamy sand (pH 5.6, 0.9% organic carbon, 6% clay) and a Webster sandy loam (pH 7.3, 3.9% organic carbon, 25% clay) at four different soil moisture levels over a 31-day incubation period and an initial loading rate of about 10 μg 2,4-D per gram of soil (Ou 1984). The half-life of 2,4-D ranged from 3.9 to 9.4 days in the loamy sand and from 7.0 to 253.9 days in the sandy loam depending upon the water content of the soil at an incubation temperature of 25°C. The greatest degradation rates of 2,4-D occurred for both soils under moist conditions as opposed to dry conditions, suggesting that greater microbial activity occurred in moist as opposed to dry soils and that greater moisture content decreased the amount of bound residues in the soils.

Thirty field dissipation studies conducted in seven states using bare soils and four cropping practices over the 2-year period of 1993–1994 were used to assess the environmental fate of 2,4-D following its application as 2,4-D dimethyl amine salt and 2,4-D EHE with both liquid and granular applications (Wilson et al. 1997). The first set of studies used wheat and turf fields located in Colorado and North Carolina and pastures in Texas. The second set of studies used cornfields from Nebraska and Ohio, wheat fields from North Dakota, and pasture, bare soil and turf fields located in California. Soil half-lives ranged from 1.7 days for turf applications in North Carolina to 12.8 days to pasture fields in Texas during the first set of trials conducted in 1993 in which all applications of 2,4-D were applied as sprays. Half-lives ranged from 2.1 days (bare soil California) to 31.2 days (pasture North Dakota) in the second set of trials conducted in 1994 in which 2,4-D was applied as sprays. Slightly greater half-life ranges were observed for the granular applications as opposed to the liquid sprays, which may be due to the time required to release the herbicides into the soil matrix. Across these studies, <5% of applied 2,4-D leached further than 15 cm from the surface. Moisture content played a major role on the half-life, with higher moisture levels resulting in faster degradation. Since these compounds, and other commercial forms of 2,4-D, are converted rapidly in soil to the same anionic form, these studies were representative of 2,4-D and showed that the chemical form had little effect on the rate of dissipation.

The EPA performed an analysis of the half-life of 2,4-D in various soils depending upon whether it was applied in granular form or as a liquid concentrate (EPA 2004). The granular half-lives ranged from 5.1 to 24.6 days, with a median half-life of 11.9 days, while the concentrate form had half-lives ranging from 1.1 to 42.5 days, with a median half-life of 5.5 days (EPA 2004).

2,4-D EHE was broadcast applied as a spray at a nominal concentration of 4 lbs/acre to a forested sandy clay loam soil located in Georgia (EPA 2004). 2,4-D EHE transformed to 2,4-D, with half-lives of 1.7, 7.2, and 51 days in the protected soil (soil under the forest canopy), foliage, and leaf litter, respectively. 2,4-D EHE was only detected 2 times in exposed soil (not protected by the forest canopy) and was not detected in the exposed soil after 3 days. The half-life of the corresponding 2,4-D was 4 days in the exposed soil, 3.6 days in the protected soil, 23.5 days in foliage, and 52.2 days in the leaf litter (EPA 2004).

2,4-D is generally considered a nonpersistent herbicide; however, at very high application rates, it may be toxic to the microorganisms of some soils or require a prolonged lag period before degradation begins. In a study of 2,4-D applied to various soils representative of the major soil orders of the United States, the lag period and overall degradation rate were directly related to the application rate of 2,4-D (EPA 1980). Formulated and technical-grade 2,4-D degradation, as measured by CO_2 evolution, began around day 10 following applications of 2,4-D at 50 and 500 mg/kg; however, the lag period increased to approximately 21 days at an initial application of 5,000 mg/kg and 50 days at an application rate of 20,000 mg/kg using a Webster silty clay loam soil (EPA 1980). Almost no CO2 evolution was observed from a sandy loam over the 80-day incubation period at application rates of 5,000 and 20,000 mg/kg, and even the addition of nutrients to the soil did not stimulate degradation.

Preconditioning of organisms to 2,4-D may also increase the rate of degradation in soil. Rosenberg and Alexander (1980) reported 2,4-D added to soil inocula showed 90% degradation after 14 days, after which subsequent additions of 2,4-D was reduced by 70% after 3–4 days. In a long-term field experiment where 2,4-D was applied annually, the complete degradation time was reduced from 10 weeks after one application to 4 weeks after 19 years of annual application (Torstensson et al. 1975).

In a study of the degradation of 2,4-D in soils at different pH levels, the half-life of 2,4-D was 5–8 days in soils in the pH range of 5.0–8.5. Degradation was slower in acidic soils, with half-lives of 21 and 41 days in soils with pH 4.5 and 4.0, respectively (Torstensson 1978).

The half-life of 2,4-D applied to a sterilized soil at 4.31 µg/g and irradiated with sunlight was 68 days (EPA 2004).

Other Media. In a study of the degradation of 2,4-D in forest leaf litter from red alder, ceanothus, vine maple, bigleaf maple, or Douglas fir collected in western Oregon, 2,4-D was shown to degrade approximately 25–40% after 15 days (Norris and Greiner 1967).

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to 2,4-D depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of 2,4-D 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 2,4-D 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 limit of detections 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	0.015 mg/m^3	NIOSH 1994
Drinking water	0.078 ppb	EPA 1995a
Surface water and groundwater	0.078 ppb	EPA 1995a
Soil	0.11 µg/kg soil	EPA 1996b
Sediment	0.01 ppb (suspended sediment)	USGS 1987
Urine	0.05 ppb	Draper 1982

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

Table 5-5. Summary of Environmental Levels of 2,4-D

Media	Low	High	For more information
Outdoor air (ppbv)	0.0017	4	Section 5.5.1
Indoor air (ppbv)	No reliable data	No reliable data	Section 5.5.1
Surface water (ppb)	0.003	37	Section 5.5.2
Ground water (ppb)	0.33	50	Section 5.5.2
Drinking water (ppb)	0.0011	58	Section 5.5.2
Food (ppb)	0.03	1.69	Section 5.5.4
Soil (ppb)	8	143	Section 5.5.3

Detections of 2,4-D in air, water, and soil at NPL sites are summarized in Table 5-6.

Table 5-6. 2,4-D Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median[a]	Geometric mean[a]	Geometric standard deviation[a]	Number of quantitative measurements	NPL sites
Water (ppb)	575	412	39.6	12	9
Soil (ppb)	2,750	2,660	3.26	10	6
Air (ppbv)	No data				

[a]Concentrations found in ATSDR site documents from 1981 to 2019 for 1,854 NPL sites (ATSDR 2019). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

Levels of 2,4-D in the ambient atmosphere are generally low or below the detection limits of the analytical methods used to monitor for this substance, with the exception of areas where it is applied as an herbicide and may reach levels in the low µg/m^3 range. In areas of high use of 2,4-D in Canada, such as cultivated regions, about 40% of air samples collected contained between 0.01 and 0.1 µg/m^3 (WHO 2003). In a monitoring study of the air quality in citrus growing regions of the United States, only 1 of 880 air samples contained 2,4-D at a concentration of 4 µg/m^3 (WHO 2003).

In a study that sampled air from nine locations, both urban and rural, in the United States in 1967 and 1968, 2,4-D was detected in one urban sample in Salt Lake City, Utah at a maximum concentration of 4.0 ng/m^3 (Stanley et al. 1971). 2,4-D was not detected in the air of any of the rural areas sampled, which included locations outside of Buffalo, New York; Dothan, Alabama; Iowa City, Iowa; Orlando, Florida, and Stoneville, Mississippi. During the spraying season in Saskatchewan, Canada in 1972, the 33-day mean daily air concentrations of 2,4-D in urban Saskatoon was 600 ng/m^3, and the 47-day mean daily level was 142 ng/m^3 in Naicam (Que Hee et al. 1975).

In air samples collected in rural south-central Washington at seven and eight stations in 1973 and 1974, respectively, the average 2,4-D concentrations detected were 0.31 and 0.22 μg/m^3, respectively (Farwell et al. 1976). It was reported that the source of 2,4-D was from spray drift from nearby croplands.

In a study of 2,4-D atmospheric levels in an agricultural location in Saskatchewan, Canada where this herbicide was used extensively to treat weed infestations in cereal crops, 2,4-D was detected in 44–63% of the atmospheric samples obtained in the summer of 1989 and 33–53% of the samples obtained in the summer of 1990 (Waite et al. 2002). Mean concentrations ranged from 0.21 to 0.77 ng/m^3 in 1989 and from 0.17 to 0.49 ng/m^3 in 1990. The maximum air concentration of 2,4-D in samples in the summers of 1989 and 1990 was 3.90 ng/m^3 (Waite et al. 2002). 2,4-D detections in 1989 were attributed to atmospheric transport of wind-eroded soils from treated fields in nearby locations since this herbicide had not been applied near the sampling sites in that summer. The authors also studied the bulk atmospheric deposition of 2,4-D for both of the summers and noted that the highest deposition rates occurred during the month of June, which was the time that the majority of 2,4-D was applied in the region. The maximum bulk deposition rate was 3,550 ng/m^2-day in the summer of 1989 and 1,550 ng/m^2-day in the summer of 1990 (Waite et al. 2002).

2,4-D was detected in indoor air in a study of 13 residences following application to lawn surfaces (Nishioka et al. 2001). No 2,4-D was detected in any indoor air samples 1 week prior to application; however, widespread contamination of both the indoor air and home surfaces (e.g., carpets, floors, etc.) was noted postapplication with notable differences in levels depending upon whether the application was performed by the homeowner or a commercial contractor. Within 2 hours of homeowner application, average 2,4-D levels were approximately 9 and 4 ng/m^3 for PM10 and PM2.5 associated particle sizes, respectively, and about 4 (PM10) and 1 (PM2.5) ng/m^3 following contractor application. By day 3 postapplication, the average levels had decreased to about 3 (PM10) and 1 (PM2.5) ng/m^3 in the residences treated by the homeowner and about 2 (PM10) and 1 (PM2.5) ng/m^3 in the residences treated by the contractors. The main route of contamination was reported to be track-in practices by the homeowners and their pets.

5.5.2 Water

The widespread use of 2,4-D can result in its occurrence in surface water, groundwater, and drinking water, with concentrations typically in the µg/L range (Botre et al. 2000; USGS 2007).

According to USGS National Water Quality Assessment Program (NAWQA), which monitors groundwater and surface water across the major watersheds in the United States, 2,4-D was one of the most common substances detected in surface water during the 1992–2001 sampling period (USGS 2007). It was detected in roughly 20% of all agricultural streams and 11% of urban streams studied, but was only infrequently detected in undeveloped and mixed land use streams (USGS 2007). Annual maximum concentrations of 2,4-D ranged from 0.003 to 15 µg/L in 4,377 surface water samples obtained from the NAWQA dataset (EPA 2005a).

Over 50% of surface water samples collected from Lakes Ontario, Erie, Huron, and Superior between 1994 and 2000 had detectable concentrations of 2,4-D, with the maximum concentration measured being 0.08 µg/L. The highest concentrations were found near agricultural and urban environments where 2,4-D is used, such as the western basin of Lake Erie (Klecka et al. 2010).

In a study of California surface waters conducted between 2008 and 2011 in three urban areas that included Sacramento (SAC), San Francisco Bay (SFB), and Orange County (OC), 2,4-D was detected in 80–84% of samples collected from SAC and OC, and 66% of samples from SFB (Ensminger et al. 2013). Median concentrations for 2,4-D in SAC, SFB, and OC were approximately 0.4, 0.2, and 0.3 µg/L, respectively. During rainstorm events and increased runoff, the detection frequency and concentration increased. Median concentrations of 2,4-D in the dry season and during a rainstorm were 0.08 and 0.28 µg/L, respectively.

One day after the application of 2,4-D to 7,000 acres in the Loxahatchee National Wildlife Refuge in Florida to control the invasive plant, water hyacinth, at a rate of 4.48 kg/hectare (3.99 lbs/A), the concentration of 2,4-D in surface water in the Hillsboro Canal was 37 µg/L, which decreased to 1–4 µg/L 56 days later (Schultz and Whitney 1974). Eight hours following application of 2,4-D at a rate of 40 lbs/A to the Nickajack and Guntersville Reservoirs in Tennessee to treat invasive Eurasian watermilfoil, levels of about 5,000 µg /L were observed at the water surface and concentrations of 1,500 µg /L were observed at the root depth (Wojtalik et al. 1971). At 2 weeks postapplication, the 2,4-D content was uniformly 650 µg /L and at 1 month postapplication, it was 1 µg /L. Surface water samples collected 4–6 times annually from November 1991 to June 1995 in South Florida had a maximum 2,4-D concentration of 14 μg/L (three detections) (Miles and Pfeuffer 1997). In a study to determine the presence of pesticides in 12 surface water supply intakes in Piedmont and coastal plain regions of North Carolina that were sampled in 1995, 2,4-D was detected in 7% of samples at a concentration range of not detected to 2.42 μg/L (Holman et al. 2000).

From April to September 2007, urban river and stream samples were collected from 19 sites within 16 watersheds, including 15 sites downstream from urban lands, across Canada and analyzed for acidic herbicides (Glozier et al. 2012). 2,4-D concentrations ranged from about 0.010 to 0.60 μg/L. Increased concentrations downstream of urban centers were linked to urban use. In agricultural watersheds sampled in Ontario, Canada from 1981 to 1985, 2,4-D was detected in approximately 9, 6, and 30% of the water samples taken from the mouth of the Grand, Saugeen, and Thames river basins, respectively (Frank and Logan 1988). Mean concentrations of 2,4-D ranged from 0.01 to 0.3 μg/L in the Grand River, from 0.1 to 0.2 μg/L in the Saugeen River, and from 0.3 to 0.7 μg/L in the Thames River (Frank and Logan 1988).

In a 1990 Puget Sound Pesticide Reconnaissance Survey, 15 water samples were collected from five drainage areas that empty into the Puget Sound in Washington and were assessed for pesticide residues (EPA 1991b). 2,4-D was detected in 13 water samples at concentrations ranging from 0.077 to 0.70 μg/L.

Even though 2,4-D is expected to have high mobility in soil, it was detected in <1% of all of the groundwater wells studied from 1992 to 2001 in the NAWQA survey due to its low persistence (USGS 2007). During the NAWQA assessment from 1992 to 1996, in which 2,485 groundwater sites were sampled in 20 of the major hydrologic basins in the United States, 2,4-D was detected in 0.43% of samples, with a maximum concentration of 0.54 μg/L (Kolpin et al. 2000). At 36 U.S. golf courses sampled in 1996, 2,4-D was detected in 8 of 773 groundwater samples at a maximum concentration of 50 μg/L (Cohen et al. 1999). Maximum and mean 2,4-D concentrations of 49.5 and 1.2 μg/L, respectively, were detected in 5 of 50 groundwater samples during a national survey of pesticides in groundwater (EPA 1988).

In the National Contaminant Occurrence Database, 27 of 71 lake/reservoir stations sampled contained a mean dissolved 2,4-D concentration of 0.33 μg/L (range of 0.01–10 μg/L) (EPA 2015b). In 73 of 256 stations where other surface waters were sampled, dissolved 2,4-D was detected at a mean concentration of 0.36 μg/L (range of 0.01–15 μg/L). The mean dissolved 2,4-D in groundwater detected at 5 of 465 stations sampled was reported as 4.0 μg/L (range of 0.01–24 μg/L).

During a study of drinking water supplies in the northern Great Plains of Canada, 15 reservoirs were sampled for pesticides during a spring application period (May to August, 2003) (Donald et al. 2007). 2,4-D was detected in all 206 samples collected, with a maximum reported concentration of 1,850 ng/L (1.850 µg/L). Mean concentrations for reservoirs in Manitoba, Saskatchewan, and Alberta were 46–182, 27–254, and 12–597 ng/L (0.046–0.182, 0.027–0.254, and 0.012–0.597 µg/L), respectively. Atmospheric deposition, snowmelt, and runoff was suspected as the major environmental transport processes responsible for 2,4-D in the reservoirs. The U.S. Department of Agriculture (USDA) Pesticide Data Program (PDP) analyzed 14 groundwater samples from 14 different wells, which included 3 from school/childcare wells and 11 from private wells in 2013 (USDA 2014). 2,4-D was detected in one sample. Additionally, 2,4-D was detected in 49 of 50 finished drinking water samples at concentrations ranging from 1.1 to 84 ng/L (0.0011–0.084 µg/L) (USDA 2014). It was also detected in 49 of 50 unfinished drinking water samples at concentrations ranging from 1.1 to 99 ng/L (0.0011–0.099 µg/L). Data from the EPA National Contaminant Occurrence Database indicated that 2,4-D was identified at 60 of 415 public water systems derived from surface water sources and 52 of 3,029 public water systems derived from groundwater at mean levels of 1.18 µg/L (range of 0.1–58 µg/L) and 0.87 µg/L (range of 0.08–8 µg/L), respectively (EPA 2015b).

Rainwater collected between February and October 1996 in Gruze, Switzerland had median and maximum 2,4-D concentrations of 16 and 23 ng/L (0.016 and 0.023 µg/L), respectively (Bucheli et al. 1998).

5.5.3 Sediment and Soil

In soil samples collected from one uncultivated and one cultivated California vertisol soil, 2,4-D concentrations ranged from 8 to 143 ppb at the uncultivated site and was not detected at the cultivated site (Graham et al. 1992). In 13 agricultural soils sampled in Canada between 1987 and 1992, the concentration of 2,4-D ranged from not detected to 38 mg/kg dry weight (Webber and Wang 1995).

In sediment samples collected from Lakes Ontario, Erie, Huron, and Superior from 1994 to 2000, 2,4-D was detected in over 50% of the samples at maximum concentrations of 1.04, 0.74, 0.28, and 0.8 µg/L, respectively (Klecka et al. 2010). Sediment samples taken from the Detroit River and Lake Huron in 1978 contained detectable levels of 2,4-D; however, the concentrations weren’t quantified (Konasewich et al. 1978).

5.5.4 Other Media

During the FDA's Market Basket study that tested 234 ready-to-eat foods 37 times a year between 1982 and 1991, the 10-year average concentration of 2,4-D detected was 0.006 µg/g (Rogers et al. 1995). Levels of 2,4-D in domestic foodstuffs were determined as part of FDA's 2004–2005 Total Diet Studies series (FDA 2005). The food samples were collected between October 2003 and August 2005. 2,4-D was detected in 22 out of 96 food items analyzed for. Twenty-one out of 22 detections were reported at the detection limit of the analytical method. The mean concentrations in µg/g (ppm) reported for 2,4-D in food items were as follows: white, enriched rice, 0.00025; white bread, 0.00060; whole wheat bread, 0.00169; fruit-flavored sweetened cereal, 0.00001; shredded wheat cereal, 0.00012; raisin bran cereal, 0.00035; crisped rice cereal, 0.00006; oat ring cereal, 0.00010; turkey and rice baby food, 0.00004; cracked wheat bread, 0.00098; rice cereal baby food, 0.00003; and meatless, Chinese fried rice, 0.00015. The most frequent detections of 2,4-D were found in bread products (FDA 2005). In 1971, 2,4-D was detected in 7 of 4,638 samples of dairy milk (Duggan et al. 1983).

Following the application of 2,4-D to 7,000 acres in the Loxahatchee National Wildlife Refuge in Florida at a rate of 4.48 kg/hectare (3.99 lbs/A), 2,4-D was detected in the breast muscle and liver of Florida gallinules at concentrations of 0.30 and 0.675 mg/kg, respectively, 1 day after spraying. Four days after spraying, no 2,4-D was detected. In 60 fish sampled, 19 had detectable 2,4-D residues in muscle tissue at concentrations ranging from <0.010 to 0.162 mg/kg (Schultz and Whitney 1974).

After treatment of the Nickajack and Guntersville Reservoirs on the Tennessee River with 2,4-D in 1969, concentrations in plankton 1, 8, and 24 hours and 14, 28, 30, 120, and 160 days after application were 0.06, 0.88, 1.8, 2.6, 3.6, 2.2, 1.1, and 3.7 ppm, respectively (Wojtalik et al. 1971). Whole body concentrations of eight species of freshwater fish from the Guntersville Reservoir did not rise above the pretreatment level of <0.10 mg/kg, with the exception of gizzard shad which had concentrations of 0.34, <0.10, 0.22, and <0.10 mg/kg at 28, 60, 120, and 180 days after application, respectively.

5.6 GENERAL POPULATION EXPOSURE

The general population may be exposed to 2,4-D during and after its use in residential and recreational areas. These include application to residential lawns, golf courses, parks, cemeteries, wooded areas, and other grassy areas. Since 2,4-D is also used on aquatic weeds, swimmers may be exposed when swimming in waters treated with 2,4-D (EPA 2005a). Transport of 2,4-D into residential homes may occur from agricultural spray drift, volatilization, soil or dust resuspension, tracked in on shoes, and on clothing (Nishioka et al. 2001). 2,4-D exposure for the general population is typically at or near the level of detection (CDC 2015). The reported limit of detection values ranged from 0.2 to 20 μg/L in the biomonitoring and epidemiology studies reviewed.

NHANES uses biomonitoring to provide estimates of exposure to the civilian U.S. population. Chemicals and their metabolites are measured in subsets of participants aged 6–59 years old, meant to be a representative sample of the population. Urine measurements are reported as both the concentration in urine and the concentration corrected for urine-creatinine level, which adjusts for urine dilution. Urinary levels of 2,4-D were measured in several NHANES programs assessing exposure to subsets of the general population in the United States from years 1999–2000, 2001–2002, and 2003–2004, 2005–2006, 2007–2008, and 2009–2010 (CDC 2015). For survey years 1999–2000, 2001–2002, and 2007–2008, no geometric mean urinary concentration of the 2,4-D could be calculated because the proportion of results below the detection limit was too high to provide a valid result. The NHANES results for 1999–2010 are summarized in Tables 5-7 and 5-8 (CDC 2015). Urinary levels have remained steady over the temporal period for the age and gender groups shown in the tables and represent a broad mix of the general public.

In a study of pesticide residues collected from 1,000 adults, ranging in age from 20 to 59 years, living in the United States, 2,4-D was detected in 12% of samples at a mean concentration of <1 μg/L (Hill et al. 1995). The 95th percentile and maximum concentrations were reported as 1.8 and 37 μg/L, respectively.

Table 5-7. Geometric Mean and Selected Percentiles of 2,4-D Urine Concentrations (in μg/L) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2010

	Survey years	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
Total	1999–2000	*	<LOD	<LOD	<LOD	<LOD	1,977
	2001–2002	*	<LOD	0.220 (<LOD–0.310)	0.690 (0.560–0.880)	1.26 (1.01–1.36)	2,903
	2003–2004	0.245 (0.210–0.286)	0.230 (0.180–0.320)	0.580 (0.490–0.660)	1.10 (0.910–1.34)	1.71 (1.41–2.37)	2,488
	2007–2008	*	<LOD	0.550 (0.530–0.590)	1.06 (0.940–1.19)	1.60 (1.38–1.79)	2,587
	2009–2010	0.308 (0.275–0.345)	0.280 (0.250–0.320)	0.530 (0.470–0.600)	0.930 (0.810–1.08)	1.43 (1.12–2.02)	2,747

Table 5-7. Geometric Mean and Selected Percentiles of 2,4-D Urine Concentrations (in µg/L) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2010

			Selected percentiles (95% CI)				
Age group	Survey years	Geometric mean (95% CI)	50th	75th	90th	95th	Sample size
6–11 years	1999–2000	*	<LOD	<LOD	<LOD	1.30 (<LOD–2.40)	477
	2001–2002	*	<LOD	0.310 (0.210–0.400)	0.740 (0.550–1.13)	1.55 (1.00–2.21)	546
	2003–2004	0.266 (0.214–0.332)	0.290 (0.200–0.390)	0.670 (0.440–0.920)	1.03 (0.890–1.40)	1.88 (1.01–2.54)	309
	2007–2008	*	<LOD	0.720 (0.630–0.860)	1.44 (1.15–1.64)	1.93 (1.62–2.84)	385
	2009–2010	0.385 (0.330–0.449)	0.350 (0.290–0.440)	0.670 (0.510–0.780)	1.20 (0.860–1.58)	1.59 (1.36–2.77)	386
12–19 years	1999–2000	*	<LOD	<LOD	<LOD	1.10 (<LOD–1.60)	677
	2001–2002	*	<LOD	0.250 (<LOD–0.420)	0.690 (0.440–1.16)	1.24 (.690–1.66)	797
	2003–2004	0.256 (0.212–0.310)	0.260 (0.180–0.380)	0.580 (0.470–0.710)	1.04 (0.890–1.31)	1.66 (1.20–2.97)	714
	2007–2008	*	<LOD	0.590 (0.530–0.670)	1.29 (0.790–1.97)	2.38 (1.46–2.73)	390
	2009–2010	0.301 (0.248–0.366)	0.280 (0.240–0.330)	0.490 (0.420–0.620)	0.900 (0.660–1.05)	1.12 (0.880–2.88)	401
20–59 years	1999–2000	*	<LOD	<LOD	<LOD	<LOD	823
	2001–2002	*	<LOD	0.210 (<LOD–0.310)	0.690 (0.540–0.910)	1.27 (0.930–1.49)	1,070
	2003–2004	0.239 (0.205–0.279)	0.220 (0.170–0.300)	0.570 (0.480–0.640)	0.980 (0.840–1.35)	1.55 (1.25–2.50)	937
	2007–2008	*	<LOD	0.530 (0.490–0.570)	0.970 (0.800–1.17)	1.36 (1.22–1.78)	1,179
	2009–2010	0.288 (0.259–0.319)	0.270 (0.230–0.310)	0.500 (0.440–0.560)	0.870 (0.740–1.04)	1.33 (1.05–1.69)	1,309
≥60 years	2001–2002	*	<LOD	<LOD	0.560 (0.390–0.870)	1.26 (0.690–1.78)	490
	2003–2004	0.248 (0.205–0.301)	0.210 (0.130–0.320)	0.560 (0.470–0.680)	1.36 (1.07–1.90)	2.42 (1.66–3.67)	528
	2007–2008	*	<LOD	0.560 (0.530–0.640)	1.02 (0.840–1.12)	1.46 (1.10–2.11)	633
	2009–2010	0.349 (0.294–0.414)	0.300 (0.230–0.390)	0.590 (0.510–0.720)	1.11 (0.810–1.57)	2.08 (1.16–5.40)	651

Table 5-7. Geometric Mean and Selected Percentiles of 2,4-D Urine Concentrations (in µg/L) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2010

	Survey years	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
Gender							
Males	1999–2000	*	<LOD	<LOD	<LOD	1.10 (<LOD–1.80)	962
	2001–2002	*	<LOD	0.330 (0.220–0.490)	0.890 (0.690–1.17)	1.49 (1.26–2.03)	1,364
	2003–2004	0.276 (0.240–0.317)	0.290 (0.210–0.370)	0.630 (0.540–0.740)	1.22 (0.960–1.42)	2.12 (1.42–2.73)	1,218
	2007–2008	*	<LOD	0.610 (0.580–0.650)	1.26 (1.05–1.38)	2.11 (1.68–2.41)	1,292
	2009–2010	0.347 (0.298–0.404)	0.320 (0.270–0.370)	0.580 (0.500–0.690)	1.05 (0.810–1.47)	1.82 (1.12–4.14)	1,343
Females	1999–2000	*	<LOD	<LOD	<LOD	<LOD	1,015
	2001–2002	*	<LOD	<LOD	0.470 (0.360–0.620)	0.890 (0.670–1.21)	1,539
	2003–2004	0.219 (0.181–0.264)	0.190 (0.110–0.280)	0.490 (0.400–0.630)	0.980 (0.860–1.33)	1.48 (1.31–2.27)	1,270
	2007–2008	*	<LOD	0.500 (0.460–0.540)	0.870 (0.790–1.01)	1.28 (1.12–1.42)	1,295
	2009–2010	0.275 (0.250–0.303)	0.260 (0.220–0.300)	0.480 (0.440–0.540)	0.860 (0.740–0.950)	1.14 (.970–1.39)	1,404
Race/ethnicity							
Mexican Americans	1999–2000	*	<LOD	<LOD	<LOD	<LOD	695
	2001–2002	*	<LOD	0.250 (<LOD–0.330)	0.730 (0.610–0.890)	1.20 (.960–1.36)	743
	2003–2004	0.313 (0.256–0.383)	0.340 (0.260–0.440)	0.730 (0.610–0.840)	1.42 (1.02–1.52)	1.81 (1.23–3.53)	606
	2007–2008	*	<LOD	0.520 (0.470–0.590)	0.860 (0.790–1.00)	1.46 (0.950–2.22)	500
	2009–2010	0.276 (0.240–0.318)	0.250 (0.210–0.300)	0.470 (0.410–0.570)	0.840 (0.680–1.08)	1.23 (0.830–2.02)	602
Non-Hispanic blacks	1999–2000	*	<LOD	<LOD	<LOD	1.20 (<LOD–1.70)	520
	2001–2002	*	<LOD	<LOD	0.560 (0.420–0.890)	1.06 (0.790–1.48)	743
	2003–2004	*	0.190 (<LOD–0.290)	0.510 (0.380–0.630)	0.910 (0.750–1.22)	1.31 (0.990–1.98)	648
	2007–2008	*	<LOD	0.580 (0.530–0.630)	1.05 (0.910–1.20)	1.49 (1.23–1.97)	574
	2009–2010	0.284 (0.251–0.321)	0.260 (0.240–0.290)	0.460 (0.390–0.540)	0.790 (0.620–1.03)	1.11 (0.790–1.81)	504

Table 5-7. Geometric Mean and Selected Percentiles of 2,4-D Urine Concentrations (in µg/L) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2010

	Survey years	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
Non-Hispanic whites	1999–2000	*	<LOD	<LOD	<LOD	<LOD	589
	2001–2002	*	<LOD	0.240 (<LOD–0.360)	0.730 (0.560–0.980)	1.30 (1.01–1.66)	1,201
	2003–2004	0.254 (0.211–0.306)	0.240 (0.180–0.360)	0.590 (0.470–0.720)	1.17 (0.930–1.41)	2.00 (1.40–2.51)	1,076
	2007–2008	*	<LOD	0.560 (0.540–0.600)	1.12 (0.940–1.29)	1.61 (1.36–2.16)	1,083
	2009–2010	0.328 (0.281–0.382)	0.300 (0.250–0.370)	0.570 (0.480–0.680)	0.980 (0.830–1.20)	1.57 (1.14–2.77)	1,200

CI = confidence interval

Source: CDC 2015

Table 5-8. Geometric Mean and Selected Percentiles of 2,4-D Urine Concentrations (Creatinine Corrected) (in µg/g of Creatinine) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2010

	Survey years	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
Total	1999–2000	*	<LOD	<LOD	<LOD	<LOD	1,977
	2001–2002	*	<LOD	0.378 (<LOD–0.412)	0.700 (0.635–0.778)	1.12 (1.03–1.26)	2,901
	2003–2004	0.241 (0.203–0.287)	0.253 (0.206–0.290)	0.500 (0.423–0.610)	1.03 (0.855–1.28)	1.85 (1.42–2.50)	2,486
	2007–2008	*	<LOD	0.737 (0.667–0.779)	1.28 (1.17–1.40)	1.84 (1.65–2.12)	2,585
	2009–2010	0.321 (0.286–0.360)	0.301 (0.272–0.329)	0.500 (0.458–0.573)	0.983 (0.846–1.19)	1.55 (1.30–2.12)	2,747
Age group							
6–11 years	1999–2000	*	<LOD	<LOD	<LOD	1.32 (<LOD–2.24)	477
	2001–2002	*	<LOD	0.485 (0.378–0.679)	1.13 (0.825–1.35)	1.41 (1.27–1.73)	546
	2003–2004	0.323 (0.249–0.421)	0.320 (0.250–0.440)	0.744 (0.500–1.06)	1.30 (0.990–2.55)	2.55 (1.23–5.16)	309
	2007–2008	*	<LOD	0.970 (0.817–1.24)	1.65 (1.47–1.85)	2.96 (1.65–6.18)	385
	2009–2010	0.521 (0.444–0.610)	0.478 (0.411–0.531)	0.792 (0.674–1.06)	1.52 (1.21–1.74)	2.20 (1.53–3.02)	386

Table 5-8. Geometric Mean and Selected Percentiles of 2,4-D Urine Concentrations (Creatinine Corrected) (in μg/g of Creatinine) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2010

	Survey years	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
12–19 years	1999–2000	*	<LOD	<LOD	<LOD	0.593 (<LOD–1.05)	677
	2001–2002	*	<LOD	0.275 (<LOD–0.376)	0.483 (0.328–0.662)	0.662 (0.517–0.918)	796
	2003–2004	0.193 (0.160–0.232)	0.205 (0.157–0.250)	0.419 (0.328–0.460)	0.709 (0.540–0.925)	1.23 (0.837–2.35)	713
	2007–2008	*	<LOD	0.555 (0.475–0.651)	0.908 (0.778–1.05)	1.56 (0.950–2.79)	388
	2009–2010	0.258 (0.212–0.314)	0.256 (0.200–0.299)	0.358 (0.320–0.439)	0.706 (0.439–1.05)	1.05 (0.579–3.27)	401
20–59 years	1999–2000	*	<LOD	<LOD	<LOD	<LOD	823
	2001–2002	*	<LOD	0.378 (<LOD–0.412)	0.667 (0.593–0.778)	1.08 (0.806–1.29)	1,070
	2003–2004	0.227 (0.188–0.274)	0.242 (0.196–0.278)	0.452 (0.397–0.545)	0.923 (0.708–1.20)	1.48 (1.14–2.43)	936
	2007–2008	*	<LOD	0.667 (0.588–0.769)	1.17 (1.04–1.34)	1.65 (1.43–2.33)	1,179
	2009–2010	0.288 (0.259–0.321)	0.276 (0.250–0.309)	0.458 (0.418–0.507)	0.860 (0.750–0.962)	1.36 (1.00–1.88)	1,309
≥60 years	2001–2002	*	<LOD	<LOD	0.824 (0.583–1.10)	1.34 (1.00–2.16)	489
	2003–2004	0.301 (0.248–0.366)	0.310 (0.237–0.385)	0.657 (0.510–0.866)	1.54 (1.16–1.95)	3.00 (1.95–6.36)	528
	2007–2008	*	<LOD	0.860 (0.781–0.903)	1.53 (1.27–1.72)	1.96 (1.60–2.33)	633
	2009–2010	0.414 (0.356–0.480)	0.354 (0.306–0.407)	0.667 (0.548–0.812)	1.41 (0.983–1.99)	2.87 (1.49–4.49)	651

Table 5-8. Geometric Mean and Selected Percentiles of 2,4-D Urine Concentrations (Creatinine Corrected) (in µg/g of Creatinine) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2010

	Survey years	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
Gender							
Males	1999–2000	*	<LOD	<LOD	<LOD	0.667 (<LOD–1.16)	962
	2001–2002	*	<LOD	0.336 (0.272–0.412)	0.652 (0.560–0.825)	1.14 (0.979–1.39)	1,364
	2003–2004	0.227 (0.189–0.271)	0.238 (0.194–0.276)	0.473 (0.412–0.564)	0.941 (0.767–1.23)	1.80 (1.09–2.79)	1,217
	2007–2008	*	<LOD	0.596 (0.538–0.670)	1.14 (0.980–1.24)	1.63 (1.47–2.15)	1,291
	2009–2010	0.309 (0.266–0.359)	0.282 (0.242–0.323)	0.481 (0.413–0.554)	1.01 (0.707–1.57)	1.80 (1.06–3.88)	1,343
Females	1999–2000	*	<LOD	<LOD	<LOD	<LOD	1,015
	2001–2002	*	<LOD	<LOD	0.711 (0.631–0.809)	1.10 (0.933–1.26)	1,537
	2003–2004	0.256 (0.213–0.308)	0.263 (0.212–0.311)	0.522 (0.435–0.645)	1.14 (0.900–1.42)	1.85 (1.42–2.64)	1,269
	2007–2008	*	<LOD	0.854 (0.757–0.903)	1.47 (1.23–1.58)	1.91 (1.65–2.33)	1,294
	2009–2010	0.334 (0.302–0.369)	0.319 (0.288–0.355)	0.533 (0.475–0.611)	0.953 (0.862–1.10)	1.40 (1.21–1.55)	1,404
Race/ethnicity							
Mexican Americans	1999–2000	*	<LOD	<LOD	<LOD	<LOD	695
	2001–2002	*	<LOD	0.350 (<LOD–0.386)	0.720 (0.583–0.840)	1.08 (.778–1.56)	743
	2003–2004	0.287 (0.223–0.371)	0.309 (0.194–0.459)	0.593 (0.463–0.771)	1.08 (0.833–1.36)	1.54 (1.17–3.19)	605
	2007–2008	*	<LOD	0.622 (0.571–0.691)	1.15 (0.903–1.43)	1.74 (1.37–2.33)	499
	2009–2010	0.289 (0.255–0.326)	0.282 (0.255–0.300)	0.434 (0.392–0.495)	0.781 (0.565–1.11)	1.30 (.733–2.63)	602
Non-Hispanic blacks	1999–2000	*	<LOD	<LOD	<LOD	0.593 (<LOD–1.19)	520
	2001–2002	*	<LOD	<LOD	0.467 (0.349–0.583)	0.778 (0.552–0.975)	742
	2003–2004	*	0.140 (<LOD–0.194)	0.304 (0.264–0.356)	0.629 (0.461–0.815)	0.970 (0.719–1.50)	648
	2007–2008	*	<LOD	0.509 (0.457–0.596)	0.966 (0.875–1.07)	1.33 (1.12–1.75)	573
	2009–2010	0.215 (0.192–0.240)	0.195 (0.180–0.218)	0.344 (0.314–0.400)	0.628 (0.489–0.822)	1.06 (0.714–1.38)	504

Table 5-8. Geometric Mean and Selected Percentiles of 2,4-D Urine Concentrations (Creatinine Corrected) (in µg/g of Creatinine) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2010

	Survey years	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
Non-Hispanic whites	1999–2000	*	<LOD	<LOD	<LOD	<LOD	589
	2001–2002	*	<LOD	0.412 (<LOD–0.455)	0.769 (0.667–0.894)	1.25 (1.05–1.40)	1,200
	2003–2004	0.263 (0.213–0.326)	0.269 (0.226–0.318)	0.539 (0.434–0.665)	1.13 (0.941–1.46)	2.34 (1.54–2.73)	1,075
	2007–2008	*	<LOD	0.780 (0.737–0.871)	1.36 (1.17–1.55)	2.00 (1.60–2.49)	1,083
	2009–2010	0.357 (0.308–0.414)	0.328 (0.288–0.384)	0.547 (0.485–0.644)	1.10 (0.897–1.40)	1.79 (1.35–3.02)	1,200

CI = confidence interval

Source: CDC 2015

In the CTEPP study, the exposures of 135 preschool children and their adult caregivers to 2,4-D at their homes in North Carolina and Ohio were examined in 2000 and 2001 (Morgan et al. 2008). Monitoring was performed over a 48-hour period, and personal (hand wipes and food) and environmental (air, soil, and dust) samples were collected. 2,4-D was detected in all types of environmental samples, with the highest frequency in carpet dust samples at 83% (median concentration of 47.5 ng/g) and 98% (median concentration of 156 ng/g) in North Carolina and Ohio, respectively. Detection frequencies in North Carolina and Ohio were 38 and 49% (maximum concentrations of 3.7 and 2.0 ng/m^3) for indoor air, 19 and 34% (maximum concentrations of 1.7 and 3.2 ng/m^3) for outdoor air, and 17 and 45% (maximum concentrations of 30.5 and 13.3 ng/g) for soil, respectively. Maximum concentrations of 2,4-D in personal exposure samples for adults in North Carolina and Ohio were 0.02 and 0.1 ng/cm^2 for hand wipes and 4.0 and 3.7 ng/g for solid food, respectively. 2,4-D was detected in >85% of the total samples collected. The median 2,4-D urinary concentrations in adults were 0.7 ng/mL for both North Carolina and Ohio residents. Morgan (2015) examined urinary levels of 2,4-D and other pesticide biomarkers and compared sociodemographic and lifestyle factors with exposure levels. Geometric mean urinary levels of 2,4-D (0.80 ng/mL [µg/L]) in urine of younger adults aged 20–35 years were significantly higher ($p=0.0025$) when compared to levels (0.54 ng/mL [µg/L]) in older adults aged 36–49 years. The study also indicated that sweet/salty snack consumption, time spent outside the home, and creatinine levels were significant ($p<0.05$) predictors of urinary 2,4-D levels.

Indoor air, outdoor air, and urine samples were analyzed for 2,4-D in a study assessing the exposure of 20 home gardeners and 19 bystanders living within the household using the product. (Harris et al. 1992). The homeowners were divided into groups that wore protective and non-protective clothing and applied both a granular and liquid formulation. The protective apparel group applying liquid 2,4-D reported no 2,4-D in air samples collected outside and only one detection at 6.0 μg/m^3 in indoor air. The protective group using granular 2,4-D reported no 2,4-D in indoor samples and three detections in outdoor air, with a mean concentration of 2.9 μg/m^3. No 2,4-D was detected in the urine of bystanders in either protective group. Among the applicators, three had detections in urine at total concentrations of 108, 63, and 38 μg/person in 4 days, and these were all attributed to the applicator removing their gloves at some point during application. Analysis of urine samples collected from home gardeners 96 hours after application showed 2,4-D total body doses ranging from below detection to 0.0071 mg/kg of body weight. The total mean 2,4-D urine concentration of applicators using liquid and granular formulations were 203.6 and 18.8 μg/person in 4 days, respectively. Bystanders in both non-protective groups had no 2,4-D detections in urine. The highest exposures were found in the group wearing non-protective apparel and were associated with spills of the liquid formulation and dermal contact with the herbicide. There is a chance that bystanders could be exposed from treated turf grass immediately following application, although it has been shown that this may be <6% of the original amount of 2,4-D used.

Workers may be exposed to 2,4-D during mixing, loading, and applying, for both crop and non-agricultural uses (EPA 2005a). Families of workers may also be exposed to 2,4-D through home surfaces contaminated from contact with an applicator’s hands or clothing. Deposition of 2,4-D contaminated dust or aerial dispersion from field spraying may also lead to surface contamination (Arbuckle et al. 2006).

In a biomonitoring study of exposure to 2,4-D in farm families with licensed applicators in Minnesota and South Carolina, 24-hour urine 2,4-D concentrations were collected 1 day before through 3 days after application (Alexander et al. 2007). For applicators (n=34), spouses (n=34), and children 4–17 years old (n=53), the median urine 2,4-D concentrations pre-application and 1 day after application were 2.1 and 73.1 μg/L, below the limit of detection and 1.2 μg/L, and 1.5 and 2.9 μg/L, respectively. At baseline, 2,4-D was detectable in the urine of 70% of the applicators, 41% of the spouses, and 62% of the children. The mean urine 2,4-D concentration in applicators and spouses the day before application, the day of application, 1 day after application, 2 days after application, and 3 days after application were 3.8 and 1.0, 29.1 and 1.0, 64.2 and 1.3, 45.3 and 1.4, and 28.3 and 1.3 μg/L, respectively. During and postapplication concentrations for applicators were substantially higher than baseline concentrations. Applicators who wore gloves to prevent direct skin contact had consistently lower urine 2,4-D concentrations, with the mean concentration for applicators not wearing gloves >7 times greater (236 compared to 44 μg/L). Exposure to spouses was determined to be primarily attributable to the level of contact with the application process, including their presence during mixing or application of 2,4-D. The geometric mean urinary levels of 2,4-D in 69 herbicide applicators were 7.8 and 25 μg/L prior to 2,4-D application and 1 day following application, respectively (Thomas et al. 2010a, 2010b). The mean absorbed dose estimated for 14 2,4-D broadcast and spray applications was 0.0027±0.0044 mg/kg/day. The mean absorbed dose accounts from exposures from all sources, including application (dermal and inhalation) plus dietary ingestion and contact with 2,4-D containing surfaces in the home or farm.

In a study of repeated pesticide exposure to migrant and seasonal farmworkers in North Carolina, urine samples were collected from 196 farmworkers four times at monthly intervals in 2007 (Arcury et al. 2010). 2,4-D had at least one detection in 98% of farmworkers, and 86.7% had multiple detections.

While direct contact with 2,4-D during mixing, loading, application, or cleaning is the primary route of exposure for individuals living on a farm, indirect sources may also contribute. This includes contact with contaminated surfaces within the home (Arbuckle et al. 2006). In a biomonitoring study performed May through July 1996 to identify potential sources of 2,4-D exposure for families on farms, residues in drinking water and surface swipes of commonly touched surfaces with 32 Ontario farm homes were measured and compared to urinary concentrations found in applicators, spouses, and children. Surfaces tested were exterior door handles, refrigerator handles, kitchen faucet, washing machine knobs, bathroom faucet, wash-up faucet, telephone, toilet handle, and tractor steering wheel. 2,4-D was detected on all measured surfaces, with the highest levels found on the washing machine knob, wash-up faucet, and tractor steering wheel. For urine samples collected before application of 2,4-D, 66% of applicators, 44% of spouses, and 46% of children had a concentration ≥1 μg/L of 2,4-D, suggesting that 2,4-D used in previous seasons may be tracked indoors and persist on home surfaces. Mean concentrations of drinking water suggested that this is not an important route of exposure, as only 1% of homes had detectable levels of 2,4-D (Arbuckle et al. 2006).

A study was conducted measuring the levels of pesticides in urine and hand wipes among 24 farmer and 23 non-farmers in Iowa in the spring and summer of 2001 (Curwin et al. 2005a). Urine and hand wipe samples were collected from each person on two occasions, approximately 1 month apart. 2,4-D urinary concentrations were significantly higher in farmers who applied 2,4-D (mean of 13 μg/L), compared to farmers who had it commercially applied (mean of 1.6 μg/L), farmers who did not apply it (mean of 0.48 μg/L), and non-farmers (mean of 0.29 μg/L). It was shown that 2,4-D urine levels may be associated with time since application, amount of 2,4-D applied, and number of acres to which it was applied. None of the 21 hand wipe samples collected had detectable 2,4-D residues. Urinary levels of 2,4-D were measured in corn farmers from Iowa over the period of March to November 2002 and 2003 (Bakke et al. 2009). Statistically significant increases in 2,4-D levels were observed during the planting season as compared to pre-planting and the offseason; however, differences remained significant even after the exclusion of urine samples obtained within 7 days of application, suggesting that exposure can continue well after application.

Curwin et al. (2005b) conducted a study of agricultural pesticide contamination in 25 farm homes and 25 nonfarm homes in Iowa by collecting air, surface wipe, and dust samples between May and August of 2001. Samples from 11 homes (5 farm homes and 6 nonfarm homes) were taken for 2,4-D detection. 2,4-D was found in 100% of farm and nonfarm dust samples, with concentrations of 0.0041–1.9 and 0.00099–5.3 ng/cm2, respectively. In farm and nonfarm homes, 2,4-D adjusted mean concentrations in dust were highest in the entryway, 850 and 740 ng/g, respectively, while in the child’s bedroom, the mean concentrations were 660 and 450 ng/g, respectively. All outdoor air (n=98) and indoor air samples (n=99) were below the limit of detection. Of the 82 house wipe and 48 vehicle wipe samples, 2,4-D was below the detection limit for all samples. This study is another example that agriculturally used 2,4-D may be an important source of home contamination.

In workers spraying 2,4-D in wheat fields, concentrations detected in 165 urine samples from 34 workers ranged from 35 to 400 μg/L (Aprea et al. 1997).

A summary of urinary concentrations 2,4-D in workers is presented in Table 5-9.

Table 5-9. Measured 2,4-D Urine Concentrations for Workers

Occupation	Number of samples	Geometric mean (μg/L)	Notes	Reference
Farmer (applicator)	34	3.8, 29.1, 64.2, 45.3, and 28.3	Day before, day of, 1 day after, 2 days after, and 3 days after application, respectively	Alexander et al. 2007
Herbicide applicator	69	7.8 and 25	Prior to and 1 day after application, respectively	Thomas et al. 2010a, 2010b
Farmer (applicator)	48	13		Curwin et al. 2005a
Sprayers in wheat fields	165	35–400 (range)	34 workers sampled	Aprea et al. 1997

The National Occupational Exposure Survey (NOES) conducted by NIOSH in 1983 estimated that 471 workers employed at 94 facilities were potentially exposed to 2,4-D in the United States (RTECS 2009). The NOES database does not contain information on the frequency, concentration, or duration of exposure; the survey provides only estimates of workers potentially exposed to chemicals in the workplace.

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

A susceptible population will exhibit a different or enhanced response to 2,4-D than will most persons exposed to the same level of 2,4-D in the environment. Factors involved with increased susceptibility may include genetic makeup, age, health and nutritional status, and exposure to other toxic substances (e.g., cigarette smoke). These parameters result in reduced detoxification or excretion of 2,4-D, or compromised function of organs affected by 2,4-D.

No studies of populations unusually susceptible to 2,4-D toxicity were identified in the literature reviewed.

Studies in animals have shown that 2,4-D is eliminated from the body by active secretion into urine by means of an OAT1 carrier. This carrier protein, which is shared by many animal species including humans, was found to be developmentally-regulated in rats, as expression increased 4-fold between PND 5 and 35 in both male and female rats (Buist et al. 2002). If this were the case also in humans, neonates and/or infants could be at a higher risk for 2,4-D toxicity since lower renal clearance of 2,4-D has been associated with increased systemic toxicity of 2,4-D, as it occurs in dogs (Gorzinski et al. 1987).

A study in rats reported that undernourished pups were more vulnerable to the effects of 2,4-D (body weight, organ’s weight) than well-nourished pups (Ferri et al. 2003). A later study from the same group of investigators confirmed the results regarding body weight and reported that undernourished pups also may be more vulnerable to the hypomyelinating effect of 2,4-D (Konjuh et al. 2008).

As discussed in Section 5.6, occupational exposure to workers during mixing, loading, and application of 2,4-D will likely result in higher-than-average exposures to this substance (EPA 2005a). The EPA RED outlines the Personal Protective Equipment (PPE) requirements for 2,4-D labeling for liquids, wettable powders, and water dispersible granules as well as pure granular formulations (EPA 2005a). In general, in order to reduce exposure, mixers, loaders, applicators flaggers, and other handlers should wear longsleeved shits/pants, shoes, and socks and chemical resistant gloves. Homeowners and their families who use 2,4-D for lawn treatment also have a higher potential for exposure than people who do not apply 2,4-D to their lawns. Homeowners applying 2,4-D should follow similar labeling procedures to reduce exposure. Families of workers may also be exposed through home surfaces contaminated from contact with an applicator’s hands or clothing. In addition, families living proximal to treated fields, orchards, and managed forests/timber may have greater exposure than the general population.

Comparing urinary 2,4-D levels from the NHANES, 1999–2010, report to data from occupationally exposed workers indicates that urinary 2,4-D levels can be up to 100 times greater for workers shortly after application as compared to the general population in the 50th percentile (Alexander et al. 2007; CDC 2015; Thomas et al. 2010a, 2010b).