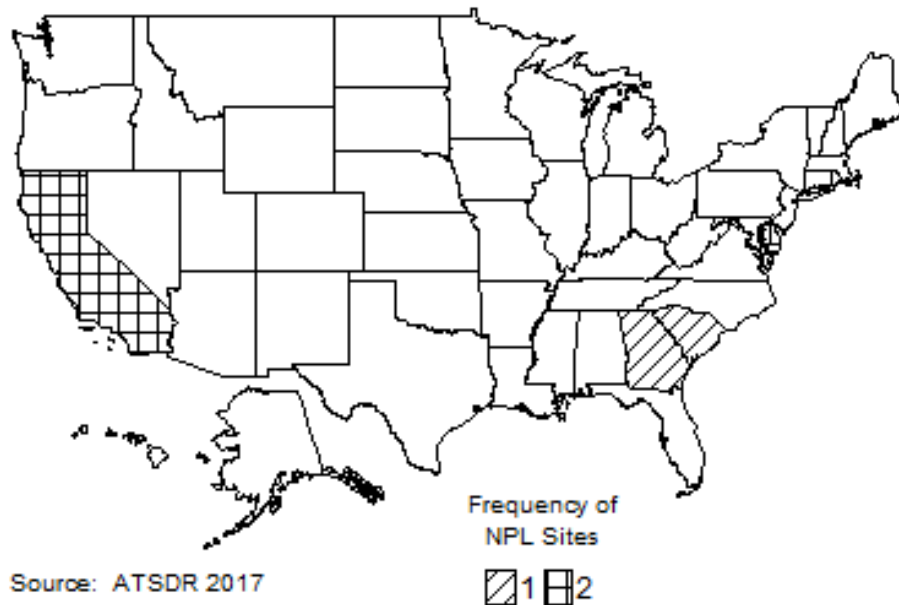


## CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

Tribufos has been identified in at least 4 of the 1,854 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2017). However, the number of sites in which tribufos has been evaluated is not known. The number of sites in each state is shown in Figure 5-1. Of these sites, all are located within the continental United States.

**Figure 5-1. Number of NPL Sites with Tribufos Contamination**



- Humans may be exposed to tribufos in food and drinking water; however, monitoring data suggest low occurrence in both of these media as tribufos is solely used as a defoliant for cotton. Non-dietary routes, such as dermal and inhalation exposure, may occur due to spray drift for populations living in cotton-growing areas.
- Workers who mix and apply tribufos to cotton plants may have dermal and inhalation exposure to this substance.
- The Henry's law constant and vapor pressure of tribufos suggest a low potential for volatilization; however, field studies have indicated that volatilization from environmental media is not negligible under hot, moist conditions that are typical during tribufos usage.
- Tribufos is unlikely to leach in soils and contaminate underlying groundwater, although it may reach surface water from runoff and erosion of treated cotton fields or from spray drift when applied aerially near a water body.
- Tribufos is stable to hydrolysis under neutral and acidic conditions; however, it is likely to hydrolyze slowly under alkaline conditions. Microbial degradation (biodegradation) is likely to be the most important transformation route of tribufos in soil, water, and sediment.

## 5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

### 5.2.1 Production

As stated previously, tribufos belongs to the organophosphate family of chemicals. Tribufos is produced commercially by reacting tributaneithiol with phosphorous trichloride in the presence of a base (Elvers et al. 1992).

Table 5-1 summarizes information on facilities that produced, processed, or used tribufos in 2017 (TRI17 2019). Toxics Release Inventory (TRI) data should be used with caution since only certain types of industrial facilities are required to report. This is not an exhaustive list.

**Table 5-1. Facilities that Produce, Process, or Use S,S,S-Tributyl Phosphorotrithioate**

State <sup>a</sup>	Number of facilities	Minimum amount on site in pounds <sup>b</sup>	Maximum amount on site in pounds <sup>b</sup>	Activities and uses <sup>c</sup>
AL	1	100,000	999,999	1, 3, 4, 7
LA	1	10,000	99,999	10

<sup>a</sup>Post office state abbreviations used.

<sup>b</sup>Amounts on site reported by facilities in each state.

<sup>c</sup>Activities/Uses:

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

Source: TRI17 2019 (Data are from 2017)

According to the EPA Chemical Data Reporting (CDR) database, in 2012, there were two manufacturers of tribufos: the Amvac Chemical Company, that manufactured 2,089,000 pounds, and the Bayer Corporation, which declared its production volume as confidential business information for 2012 (EPA 2016). Updated data from the CDR indicated that the national aggregate production volume was <25,000 pounds in 2015 (EPA 2019a). Data obtained from the National Pesticide Information Retrieval System (NPIRS) show that there are four companies that formulate tribufos into end-use products. These companies and their products are listed in Table 5-2.

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**Table 5-2. U.S. Companies Manufacturing Tribufos Products**

Company	Registered product	Active ingredients
Amvac Chemical Corporation	Folex 6 EC	70.5% tribufos
	DEF Technical Defoliant	97.9% tribufos
	DEF 6 Emulsifiable Defoliant	70.5% tribufos
Loveland Products Inc.	DFT 6 EC Cotton Defoliant	70.5% tribufos
RedEagle International LLC	Tribufos Technical	99.5% tribufos
	Tribufos 6	70.5% tribufos
Axion AG Products LLC	AX Tribufos 6	70.5% tribufos

Source: NPIRS 2019

### 5.2.2 Import/Export

Data from the CDR indicated that neither Amvac nor Bayer import tribufos into the United States from other countries; however, they do not report whether or not tribufos was exported to other nations.

### 5.2.3 Use

Tribufos is a plant growth regulator that is used exclusively as a defoliant for cotton plants in preparation for machine harvesting (EPA 2006b; Tomlin 2003). Tribufos is absorbed by the leaves and stimulates an abscission layer between the plant stem and the leaf petioles, resulting in the dropping of the entire green leaf. Tribufos is also used to reduce or prevent losses from boll rot organisms by separating the organism's habitat from the cotton crop. An estimated 4.5 million pounds of tribufos was used in 1999; tribufos was applied as a defoliant to approximately 35% of the 14 million acres of cotton fields in the United States (EPA 2006b). The USGS Pesticide National Synthesis Project estimated that approximately 2.8 million pounds of tribufos were applied to cotton crops in 2016 (USGS 2019). Tribufos is usually applied as a tank-mix for use as an emulsifiable concentrate with other defoliants via aerial spraying or groundboom spraying at an application rate of 0.50–0.75 pounds active ingredient per acre (lbs ai/A). The maximum application rate is 1.125 lbs ai/A in all states with a restricted entry interval of 7 days, but may be applied at an application rate of 1.875 lbs ai/A if used alone in California and Arizona (EPA 2000a, 2006b). The state of California restricts application of tribufos within a half-mile of residential areas.

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**5.2.4 Disposal**

The best way to dispose of tribufos is to mix the appropriate amount and apply the full amount to the cotton crops. Immediately after application, workers should remove all unused product and follow labelled instructions for disposal (CPCR 1992). Containers containing tribufos may be triple rinsed for recycling or reconditioning, if applicable. Otherwise, the container must be punctured and disposed into a sanitary landfill or by any other means approved by state and local authorities (CPCR 1992).

**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 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ  $\geq 10$  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  $\geq 25,000$  pounds of any TRI chemical or otherwise uses  $> 10,000$  pounds of a TRI chemical in a calendar year (EPA 2005).

**5.3.1 Air**

Estimated releases of 10 pounds (~0.004 metric tons) of tribufos to the atmosphere from one domestic manufacturing and processing facility in 2017, accounted for 100% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2019). These releases are summarized in Table 5-3.

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**Table 5-3. Releases to the Environment from Facilities that Produce, Process, or Use S,S,S-Tributyl Phosphorotrithioate<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>							
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
AL	1	10	0	0	0	0	10	0	10
LA		No data							
Total	1	10	0	0	0	0	10	0	10

<sup>a</sup>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.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI17 2019 (Data are from 2017)

**5.3.2 Water**

There were no estimated releases of tribufos to surface water from the one domestic manufacturing and processing facility in the 2017 TRI (TRI17 2019). This estimate included releases to waste water treatment and publicly owned treatment works (POTWs) (TRI17 2019).

Runoff, erosion of contaminated soil, and spray drift from aerial application are the main environmental fate processes that result in tribufos contamination of surface waters. Potter et al. (2003) studied the runoff potential of three defoliant, including tribufos, applied to strip and conventionally tilled cotton in a 1.9 hectare (4.7 acre) field located in south central Georgia. The runoff of tribufos applied at a rate of 0.31 kg/hectare (approximately 15–25% of the label use rate) was approximately 12.8% of the applied amount in the strip tilled plot and 14.5% of the amount applied in the conventional tillage plot following a 45-minute simulated rainfall event that occurred shortly after application.

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**5.3.3 Soil**

There were no estimated releases of tribufos to soil or through underground injection from the one domestic manufacturing and processing facility in 2017 (TRI17 2019).

**5.4 ENVIRONMENTAL FATE****5.4.1 Transport and Partitioning**

**Air.** Based on its vapor pressure ( $5.3 \times 10^{-6}$  mm Hg at 25°C), tribufos released to the atmosphere via aerial or boom spraying would be expected to exist in both the vapor and particulate phases (Eisenreich et al. 1981). Vapor-phase tribufos will react with photochemically generated hydroxyl radicals, while particulate-phase tribufos will be removed from the atmosphere by wet and dry deposition.

**Water.** Soil column leaching experiments using four different types of soils indicated that tribufos applied to the top of the columns remained within 4 cm of the surface and <1% was observed in the leachate water. Field dissipation studies in which tribufos was applied to mature cotton plants on 0.2 hectare research plots also indicated a low potential for leaching (Potter et al. 2002). Over the course of the 3-year monitoring period, tribufos was not detected in shallow groundwater wells installed in the plots or in drainage water at the outer surface of the plots that collected shallow subsurface water flow. These data suggest that tribufos is unlikely to leach in soils and contaminate underlying groundwater. The low potential for leaching is supported by monitoring studies that show that tribufos is rarely detected in groundwater. Tribufos may reach surface water from runoff and erosion flux of treated field soils or from spray drift when applied aerially or from a groundboom near a water body.

The measured Henry's Law constant of tribufos is  $2.94 \times 10^{-7}$  atm-m<sup>3</sup>/mole (see Table 4-2), which suggests that volatilization from water and soil surfaces will occur slowly. Its large soil adsorption coefficient also suggests that adsorption to soil and sediment may attenuate the rate of volatilization. Tribufos applied at 1 µg to 100 mL of seawater and aerated at 50 mL/minute was volatilized 12% after a 7-day incubation period; however, no volatilization was observed following the addition of 10 g of sediment to seawater/tribufos mixtures (EPA 1981). A study that compared the dissipation rates of tribufos applied to soils under laboratory and field conditions concluded that volatilization may not be negligible, particularly under hot and moist meteorological conditions (Potter et al. 2002). Calculated dissipation half-times (DT<sub>50</sub>) for tribufos were approximately 25 times greater in controlled laboratory studies (14.2–18.8 days)

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in which volatilization was minimal as compared to the field study for this soil (<1–1.6 days) in which volatilization could occur. Assuming that the degradation rates under both field and laboratory conditions were similar, the authors suggested that volatilization may be an important environmental fate process for tribufos applied to cotton crops. Even at the highest levels recorded in drift studies (high of 1,189 ng/m<sup>3</sup> or 0.001189 mg/m<sup>3</sup>), data indicate that the exposure is nearly 40 times lower than the intermediate-duration inhalation MRL of 0.04 mg/m<sup>3</sup>, so health effects are unlikely from an exposure scenario that involves only tribufos that volatilizes from treated cotton fields. Furthermore, tribufos has a short atmospheric half-life, and monitoring studies indicate that atmospheric levels decrease quickly due to the short half-life.

**Sediment and Soil.** Tribufos adsorbs strongly to soils and is expected to be practically immobile. The  $K_{oc}$  values of tribufos applied to a sandy soil (88% sand, 7% silt, 5% clay, 1% organic matter, pH 4.2), sandy loam (56% sand, 30% silt, 14% clay, 1.1% organic matter, pH 6.6), silt loam (17% sand, 66% silt, 17% clay, 2.9% organic matter, pH 5.9), and clay loam (21% sand, 50% silt, 29% clay, 2.2% organic matter, pH 6.4) were 12,684, 10,465, 4,870, and 9,115, respectively (EPA 1987).

**Other Media.** Tribufos does not significantly bioaccumulate in edible tissues of aquatic organisms. Bluegill sunfish exposed to tribufos at a mean concentration of 6.2 µg/L for 35 days had a bioconcentration factor (BCF) of 300 for edible tissue and a whole-body BCF of 730; a BCF of 1,300 was reported for nonedible (viscera) residues (EPA 2008). Following a 14-day depuration period, 71–88% of the tribufos residues were reported to be eliminated from the fish. Pinfish exposed to tribufos had a measured BCF value of 350 following a 96-hour static test; however, the time period may not have been long enough to reach steady state (EPA 1981). According to CalEPA (2000), multiple 5 mg/kg gavage doses of tribufos to rats resulted in no evidence of bioaccumulation; CalEPA (2000) cited an unpublished study as the source of information.

#### 5.4.2 Transformation and Degradation

**Air.** Vapor-phase tribufos in the ambient atmosphere will be degraded by reaction with photochemically generated hydroxyl radicals. A second-order hydroxyl radical rate constant of  $7.9 \times 10^{-11}$  cm<sup>3</sup>/molecule-second was estimated using a structure estimation method (EPA 2012h; Meylan and Howard 1993). This corresponds to an atmospheric half-life of approximately 1.6 hours assuming an atmospheric hydroxyl radical concentration of  $1.5 \times 10^6$  hydroxyl radicals per cm<sup>3</sup> of air and a 12-hour sunlight day (EPA 2012h). Tribufos may be susceptible to direct photolysis by sunlight, since it absorbs photons in the

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environmental ultraviolet (UV) spectrum (wavelengths >290 nm); however, it was shown to undergo direct photolysis slowly in laboratory photoreactor experiments (Woodrow et al. 1983).

**Water.** Tribufos is reported to be stable to hydrolysis under neutral and acidic conditions (EPA 2006b, 2008). Under alkaline conditions (pH 9), the half-life of tribufos was reported to be 124 days, with desbutylthio tribufos reported to be the major breakdown product (CalEPA 2004). There was no evidence of degradation when tribufos was exposed to sunlight for 30 days in a pH 5 aqueous solution (EPA 2008). Using a structure estimation method based upon molecular fragment descriptors, a hydrolysis half-life of 1.5 years was estimated at pH 7 and a half-life of 111 days was estimated at pH 9 (EPA 2012h).

The degradation of several pesticides from raw water obtained from the Little Miami River (a small river receiving industrial and farm runoff) was studied over an 8-week incubation period in sealed glass jars under sunlight and artificial light settings (Eichelberger and Lichtenberg 1971). A 10- $\mu\text{g/L}$  sample of merphos was introduced into the river water where it was subsequently converted to tribufos within 1 hour. After 1 week, only 50% of the initially present tribufos was recovered. Recovery of tribufos after 2, 4, and 8 weeks was only 30, 10, and 5%, respectively. The dissipation of tribufos in a seawater (100 mL) and sediment (10 g) mixture was studied under sterile and nonsterile conditions (EPA 1981). In the nonsterilized system, only 20% of the initially applied tribufos was present after a 5-day incubation period and it all had partitioned to the sediment column. In contrast, 77% of the initially applied tribufos was present in the sterilized system after 7 days.

The anaerobic aquatic metabolism half-lives for tribufos applied at a rate of 1.1 mg/kg to a flooded silty clay pond sediment (0.8% sand, 41.5% silt, 57.7% clay, 3.1% organic matter, pH 7.3) were 180 and 120 days in two separate experiments (EPA 2008). The only reported metabolite was 1-butane sulfonic acid.

**Sediment and Soil.** EPA (2006b) reported an aerobic soil metabolism half-life of 745 days (EPA 2006b) and the California Department of Pesticide Regulation reported an aerobic soil metabolism half-life for tribufos of 198 days (CalEPA 2004). The aerobic soil degradation study used by EPA (2006b) was a sandy loam (58% sand, 27% silt, 15% clay, 3.8% organic matter, pH 6.8) and  $^{14}\text{C}$  labeled tribufos was applied at a nominal rate of 7 ppm and incubated in the dark at 25°C for 360 days (EPA 1991c). Tribufos was 97.7–100.2% of the applied radioactivity immediately after application and declined to 62.3–66.8% after 360 days. Methyl-des butylthio tribufos was identified as the only extractable metabolite, reaching 0.8–1.2% of the applied radioactivity after 181 days. Volatile organics represented



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2.9–3.9% of the radioactivity at the end of the experiment and  $^{14}\text{CO}_2$  was 2.9–7.0% of the applied radioactivity at the end of the incubation period. Unextractable compounds represented 15.4–18% of the radioactivity at 360 days and the material balance range was 91–108.9%. The calculated half-life was reported to be of limited value since it involves extrapolation well beyond the time limits of the incubation period. The same soil was employed to test the persistence of tribufos under anaerobic conditions.  $^{14}\text{C}$ -labeled tribufos was applied at a nominal rate of 7 ppm and incubated in the sandy loam for 60 days under nitrogen-rich anaerobic conditions (EPA 1990d). At the end of the study, 73.0–84.4% of the radioactivity was recovered as tribufos. An anaerobic soil metabolism half-life of 389 days was calculated; however, it was of limited value since it exceeds the incubation period and no positive controls were used.

Other laboratory degradation and field dissipation studies suggest that tribufos is not as persistent as the previous studies would suggest. Potter et al. (2002) examined the dissipation of tribufos under controlled laboratory and field conditions using four soils used to grow cotton that were acclimated to tribufos. Using a soil spiking application rate of 1 ppm, the  $\text{DT}_{50}$  values under controlled laboratory conditions ranged from approximately 1 to 19 days using a nonlinear fitting procedure. Half-lives of about 5–16 days were calculated using data from the first 28 days of the incubation period and a linear fitting procedure.

The length of incubation effects half-life calculations. Longer half-lives (70–109 days) were calculated when data for the entire incubation period (666 days) were used; however, isolating soils for this length of time is expected to have a negative impact on microbial communities responsible for degradation of the substance. Moreover, the degradation of many pesticides in soil is biphasic, with an initial rapid degradation period over the course of the first few weeks and a gradual decline in the rate of degradation over longer incubation times. This aging process is often observed for pesticides such as DDT that adsorb strongly to soils and eventually become sequestered in the soil, which decreases its bioavailability to microorganisms (Alexander 1995; ATSDR 2002). The concentration versus time profile resembles a “hockey-stick” type outline with relatively rapid degradation observed initially followed by a flattening of the curve over long periods of time (Alexander 1995).

Potter et al. (2002) concluded that an appropriate value for the  $\text{DT}_{50}$  or the half-life of tribufos in acclimated soils maintained at its field capacity and a temperature of 29°C should be on the order of 5–20 days. A field dissipation study conducted on a 0.2-hectare plot located in Tifton, Georgia had a calculated  $\text{DT}_{50}$  value that was about 25 times lower (0.6 days) than the laboratory values for this soil

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(14.2–18.8 days). It should be noted that this field had also been amended with an application of poultry litter 1 year prior to the experiments conducted. Although some of the dissipation was attributed to runoff from rain events during the monitoring period, the authors also assumed that some loss was due to volatilization from the soil plot and that this fate process should be included in model simulation exercises when evaluating the environmental fate of tribufos (Potter et al. 2002). The shorter persistence times in this study as compared to the study submitted for the registration of tribufos may be due to the lower application rates used and the properties of the soils. Each of the soils used in the findings by Potter et al. (2002) had been exposed to tribufos during its application to cotton crops in prior years, whereas the soil used in the registration study does not appear to have been acclimated to tribufos.

The shorter dissipation times in soils acclimated to tribufos appear to be supported by data submitted by the Bayer Crop Science Corporation to the EPA High Production Volume Challenge Program. In the Robust Summary submitted by Bayer, the rates of aerobic biodegradation of  $^{14}\text{C}$ -labeled tribufos in five cotton-growing soils obtained from Georgia, Mississippi, California, Texas, and Arkansas were reported. Tribufos applied at the maximum application rate of 1.9 pounds per acre (approximately 1 ppm for a 6-inch depth with soil density  $1.5 \text{ g/cm}^3$ ) had half-lives of 9.8, 30.3, 99, 143.6, and 173.3 days in the soils from California, Texas, Georgia, Arkansas, and Mississippi, respectively (Bayer 2008). Degradation was measured by  $\text{CO}_2$  evolution and appeared to be correlated with the pH of the soil. Soils with  $\text{pH} > 6.3$  had greater  $\text{CO}_2$  evolution as compared to soils with lower pH. The amount of  $^{14}\text{CO}_2$  evolution at the end of the experiments ranged from 37.6% in the Mississippi soil to 72.3% in the Texas soil.

The large differences in the apparent degradation times of tribufos in these studies may be due to the higher application rate used in the registration study, which may have resulted in toxicity to the microorganisms or a prolonged adaptation period. The nominal application rate was 7 times greater in the registration study than the other studies. Moreover, the soils used in the field studies by Potter et al. (2002) and Bayer (2008) were reported to have been previously exposed to tribufos in preceding planting seasons, suggesting acclimated microorganisms. It is unclear whether the sandy loam used in the registration process had been previously exposed to tribufos. The 745-day half-life appears to be an outlier considering the data reflected in the laboratory and field studies by Potter et al. (2002).

Tribufos was stable in a soil photolysis experiment in which it was incubated at a fortification level of 9.2 ppm in a sandy loam soil (48.02% sand, 49.65% silt, 2.33% clay, 1.45% organic matter, pH 6.6) and irradiated for 30 days with natural sunlight in Kentucky from February 4, 1988 through March 5, 1988 (EPA 1988).

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**5.5 LEVELS IN THE ENVIRONMENT**

Reliable evaluation of the potential for human exposure to tribufos depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of tribufos 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 tribufos 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<sup>a</sup>**

Media	Detection limit	Reference
Air	0.10 ng/m <sup>3</sup>	Majewski et al. 1998
Drinking water	0.0033 µg/L	EPA 2012g
Surface water and groundwater	0.00946 µg/L	CDFA 2013
Soil	0.01 mg/kg	EPA 2014
Sediment	0.01 mg/kg	EPA 2014
Whole blood	27 ppt	Kuklenyik 2009

<sup>a</sup>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 Tribufos**

Media	Low	High	For more information
Outdoor air (ppbv)	0.0021	0.47	Section 5.5.1
Indoor air (ppbv)	No data	No data	
Surface water (ppb)	Not detected	0.01	Section 5.5.2
Ground water (ppb)	Not detected	Not detected	Section 5.5.2
Drinking water (ppb)	Not detected	0.07	Section 5.5.2
Food (ppb)	Not detected	2,000	Section 5.5.4
Soil	No data	No data	

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

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

Medium	Median <sup>a</sup>	Geometric mean <sup>a</sup>	Geometric standard deviation <sup>a</sup>	Number of quantitative measurements	NPL sites
Water (ppb)			No data		
Soil (ppb)	412,000	222,000	5.68	2	2
Air (ppbv)			No data		

<sup>a</sup>Concentrations found in ATSDR site documents from 1981 to 2015 for 1,854 NPL sites (ATSDR 2017). 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

Since tribufos is used exclusively as a cotton defoliant and has a short atmospheric half-life, it is usually only detected in ambient air in cotton-growing regions where it has been applied. Fifty meters from a cotton field that was treated with the defoliant, tribufos was detected at levels of 1,189 ng/m<sup>3</sup> (Hermann and Seiber 1981). These levels dropped to 450 and 24 ng/m<sup>3</sup> at 24 and 72 hours post treatment, respectively. Tribufos was also detected in air samples at a maximum concentration of 6,080 ng/m<sup>3</sup> collected at a second cotton field being treated with the defoliant merphos. Tribufos was detected at levels ranging from 2.7 (detection limit) to 87.4 ng/m<sup>3</sup> at 10 residential locations in Kern County, California near a cotton field being treated with defoliants (Kilgore et al. 1984). Two weeks postapplication, tribufos was detected at its detection limit in only 1 out of 40 air samples obtained in these 10 locations. Tribufos was detected in 10% of the air samples collected from a research vessel traveling the Mississippi River from New Orleans, Louisiana to St. Paul, Minnesota at a maximum concentration of 0.04 ng/m<sup>3</sup> (Majewski et al. 1998).

Tribufos was detected in 6 out of 36 samples of air obtained from urban communities in California at a mean concentration of 1.3 ng/m<sup>3</sup> and in 121 out of 125 samples of air from rural communities in high-use agricultural areas at a mean concentration of 64 ng/m<sup>3</sup> (Lee et al. 2002). Tribufos was not detected in air samples that were collected in Parlier, California during a 12-month monitoring study of 40 pesticides conducted by the California Department of Pesticide Regulation to determine residential exposure to pesticides for persons living in agricultural communities in the San Joaquin Valley near Fresno, California (CalEPA 2009; Wofford et al. 2014). Tribufos was detected in the ambient air of four

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sampling locations in Monterey, California at a mean concentration of 68 ng/m<sup>3</sup> (maximum=340 ng/m<sup>3</sup>) from September to November 1987 (Baker et al. 1996).

### 5.5.2 Water

Due to its tendency to adsorb strongly to soil surfaces, tribufos is not expected to leach to lower soil horizons and contaminate underlying groundwater in the cotton fields where it was applied. Tribufos was not detected in 569 wells that were sampled in North America (California and Texas) from 1984 to 1988 based upon data from the USGS Pesticides in Groundwater Database (Barbash and Resek 1996; EPA 1992e, 2006b). Tribufos was not detected in 465 wells sampled in 16 counties (Colusa, Fresno, Kern, Kings, Los Angeles, Madera, Merced, Orange, Riverside, San Bernardino, San Diego, San Mateo, Santa Cruz, Stanislaus, Tulare, and Ventura) located in California (CalEPA 2004). Tribufos was identified, not quantified, in one groundwater sample obtained during a monitoring study in 28 counties in California (Cohen 1986).

Winchell and Snyder (2014) compared the levels of various pesticides in drinking water monitoring studies to levels predicted using EPA Tier 1 and Tier 2 modelling approaches. The highest estimated drinking water concentration for tribufos using the Tier 2 linked programs, Pesticide Root Zone Model/Exposure Analysis Modeling System (PRZM/EXAMS), was 14 µg/L, which was about 3 orders of magnitude larger than the maximum measured value observed from drinking water monitoring studies (0.016 µg/L) from 12 unspecified sites monitored for 1–2 years with 11–37 samples obtained per year. This result was consistent with data from the other pesticides discussed in the study whereby predicted values greatly exceeded observed concentrations from monitoring studies. Tribufos was detected in 12 out of 12 raw drinking water and 11 out of 12 filtered drinking water samples at a median level of 0.02 µg/L, collected in Cairo, Egypt near a location where it was being used as a cotton defoliant (Potter et al. 2007). Tribufos was monitored for during the Fourth UCMR, which monitors the frequency and level of occurrence of 30 unregulated contaminants in the nation's public water systems between 2018 and 2020. Data from the July 2019 summary indicated that tribufos was detected in 2 out of 11,829 samples above the minimum reporting level of 0.07 µg/L (EPA 2019b). It was only detected above the minimum reporting level in 2 out of the 2,342 public water systems that reported results.

Tribufos was detected in 2 out of 810 surface water samples collected from 1991 to 2003 in the state of California at the detection limit 0.01 µg/L (CalEPA 2004). Tribufos was not detected in water samples

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analyzed from 2000 to 2005 in the Clackamas River basin in Oregon (USGS 2008). Tribufos was not detected in seven discrete water samples collected from the Potomac River basin (Kolpin et al. 2013).

Tribufos was detected in fogwater samples at concentrations of 250 ng/L (0.250 ppb) in Parlier, California and 800 ng/L (0.800 ppb) in Corcoran, California (Glotfelty et al. 1987).

### 5.5.3 Sediment and Soil

Any tribufos that is applied aerially or by boom spraying that is not intercepted by the cotton plants may reach the underlying soil surface. In a study of six plots of soil used to grow cotton, tribufos was applied at a rate of 0.3 kg/hectare (Potter et al. 2002). Using the measured application rate and the concentration of tribufos in the upper 2 cm of the soil, it was estimated that between 5.3 and 49% of the applied tribufos reached the soil surface. The highest value was obtained for a plot where the cotton plants were already partially defoliated and the authors suggested that the tribufos fraction that typically reaches the soil surface ranges from about 8 to 24% of the initially applied amount (Potter et al. 2002).

Sediment samples obtained from the Lake Olathe watershed and Cedar Lake located in northeast Kansas had no positive detections for tribufos (n=5 for both lakes) at a detection limit of 0.20 µg/kg (USGS 2002).

### 5.5.4 Other Media

Since tribufos is applied exclusively to cotton crops, it is rarely detected in food items, although exposure to tribufos can occur from residues present in cottonseed oil or meal or as a result of consumption of livestock that may have been fed cotton gin-byproducts, cottonseed hulls, or cottonseed meal. A field test in which tribufos was applied at the maximum application rate resulted in average tribufos residues in cottonseed, cottonseed meal, hulls, crude cottonseed oil, and refined cottonseed oil of 7.266, 0.065, 1.043, 0.581, and 0.213 ppm, respectively (EPA 2000a)

Data from the United States Department of Agriculture (USDA) 2014 Pesticide Data Program report showed that tribufos was not detected in 2,341 samples of fruits or vegetables (USDA 2016b). There were no detections in apples (n=177); blueberries, fresh (n=354); blueberries, frozen (n=5); celery (n=348); grape juice (n=531); strawberries (n=176); summer squash (n=270) sweet corn, fresh (n=78); sweet corn, frozen (n=12); or watermelon (n=390).

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The Food and Drug Administration (FDA) conducts a Total Diet Study in which food items are analyzed 4 times annually, once in each of the major geographical regions of the country (west, north central, south, and northeast). Each round of sampling is referred to as an individual market basket survey and for each market basket survey, samples of selected food and beverages are obtained from cities within the region. Tribufos was detected at a concentration of 0.0060 ppm in 1 out of 44 samples of potato chips analyzed during the FDA Total Diet Market Basket Surveys conducted in 1991–2003 and 2003–2004 (FDA 2006). It was also detected at trace levels (0.0003 ppm) in one of four samples of catfish, pan cooked with an unspecified oil. It was not detected in any of the other food items in this survey. Older Total Diet Studies also suggest that tribufos is rarely detected in food items. It was identified once in an unspecified number of potato samples analyzed during the 1980–1982 Market Basket Survey (Gartrell et al. 1986). It was not detected in any of the other 12 food items in this survey. Tribufos was detected in 2 out of 6,391 samples of U.S. domestic agricultural commodities at concentrations of 0.50 and >2.0 ppm in FDA studies conducted from 1981 to 1986; it was not detected in 1,239 imported agricultural commodities (Hundley et al. 1988). According to data from the FDA Pesticide Program Monitoring Database, tribufos was not detected in any domestic or imported foods (n=6,704) analyzed in 2013 (FDA 2013).

Tribufos was detected on cotton bolls and other parts of the plant after application. Levels of tribufos on cotton bolls were 3.91 and 2.36  $\mu\text{g/g}$  (ppm) following application by ground and aerial spraying, respectively (CalEPA 2000). These levels decreased to around 0.1  $\mu\text{g/g}$  (ppm) 2 weeks postapplication. In 2001, the FDA collected a total of 478 domestic and 67 imported animal feed samples and analyzed these items for pesticide residues (FDA 2001). Tribufos was detected in six feed samples at a concentration range of 0.030–0.150 ppm and a median value of 0.074 ppm.

### 5.6 GENERAL POPULATION EXPOSURE

Tribufos is used to defoliate cotton plants; it is not for residential use or other non-occupational uses. A 2000 human health risk assessment for tribufos published by the EPA Health Effects Division (HED) concluded that the primary route of exposure to tribufos for the general public is through the ingestion of food (EPA 2000a). Inhalation exposure to tribufos is expected to be negligible for the general population, with the exception of those persons who reside near cotton fields that are treated with tribufos. Since tribufos is rarely detected in groundwater or drinking water, this is not considered an important exposure pathway for the general population.

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Tribufos residues that may be present in cottonseed oil or cottonseed meal could be directly ingested, or exposure could result from ingestion of meat or milk products from livestock that are fed cottonseed products. One sample of catfish that was pan-cooked with an unspecified oil tested positive for tribufos and 1 out of 44 samples of potato chips had quantifiable levels of tribufos (6 samples had trace levels) in the FDA Total Diet Market Basket Surveys conducted in 1991–2003 and 2003–2004 (FDA 2006). No other samples tested positive for tribufos. EPA (2006b) estimated acute and chronic dietary intakes (99.9<sup>th</sup> percentiles) of 0.050 and 0.003 µg/kg/day for the U.S. population calculated using the Dietary Exposure Evaluation Model (DEEM). The DEEM uses food consumption data from the USDA Continuing Survey of Food Intakes (CSFII) and anticipated tribufos residues on food items to estimate exposure.

Gunderson (1988, 1995a, 1995b) employed data from the 1982–1984, 1984–1986, and 1986–1991 Total Diet Market Basket Surveys to estimate the mean dietary intakes of selected pesticides, including tribufos, in the U.S. general population. The mean daily intakes for tribufos in µg/kg/day for different age and gender groups are provided in Table 5-7. Tribufos levels in the food commodities used to derive these intakes were all well below the current EPA tolerances, which are 0.01–0.15 ppm for milk and animal meats and 40 ppm in cotton gin byproducts (EPA 2015).

**Table 5-7. Mean Daily Intakes of Tribufos (µg/kg/day) for the U.S. Population**

	1982–1984 Market Basket Surveys <sup>a</sup>	1984–1986 Market Basket Surveys <sup>b</sup>	1986–1991 Market Basket Surveys <sup>c</sup>
6–11 Months old	<0.0001	<0.0001	<0.0001
2 Years old	0.0004	0.0002	0.0001
14–16 Years old, female	0.0002	0.0001	<0.0001
14–16 Years old, male	0.0002	0.0001	<0.0001
25–30 Years old, female	0.0001	0.0001	<0.0001
25–30 Years old, male	0.0001	0.0001	<0.0001
60–65 Years old, female	<0.0001	<0.0001	<0.0001
60–65 Years old, male	<0.0001	<0.0001	<0.0001

<sup>a</sup>Gunderson 1988.

<sup>b</sup>Gunderson 1995a.

<sup>c</sup>Gunderson 1995b.

Workers who apply tribufos to cotton plants are expected to receive greater exposure through dermal and inhalation routes than the general population. Total daily, seasonal, and lifetime exposure estimates by



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the dermal and inhalation routes for agricultural workers have been summarized in the risk characterization for tribufos document compiled by the California Department of Pesticide Regulation and are reproduced in Table 5-8 (CalEPA 2004). Exposure to tribufos tends to be seasonal since cotton defoliation is generally performed on mature bolls approximately 10–14 days prior to the anticipated harvest (Barber et al. 2013). Although harvest timing of cotton in the United States differs by region, it is typically performed in fall (September–November) (USDA 2010). However, the harvest may also extend into December or early January in some states. Mixers/loaders stock the aircraft with tribufos, while flaggers stand at the end of the fields to provide the pilot with a flight path. Field workers who enter treated fields may be dermally exposed to treated surfaces in the area where they are working. For tribufos, a restricted entry interval (REI) of 7 days has been established for postapplication activities including raking, picking, tramping, and module builder operations (EPA 2000a).

**Table 5-8. Estimated Occupational Exposure Scenarios for Tribufos**

Job category	Absorbed daily dose (ADD) <sup>a</sup>	Seasonal average daily dose (SADD) <sup>b</sup>	Lifetime average daily dose (LADD) <sup>c</sup>
	µg/kg/day		
<b>Handlers</b>			
Mixer/loader (aerial)	4.6	2.1	0.15
Pilot	5.1	2.4	0.17
Flagger	4.4	2.1	0.14
Mixer/loader (ground)	8.5	4.0	0.28
Applicator (ground)	0.7	0.3	0.02
<b>Field workers</b>			
Irrigators/weeders (4 days)	25.5	11.9	0.84
Irrigators/weeders (7 days)	11.3	5.3	0.37
Picker operator	5.0	2.3	0.17
Module build operator	1.9	0.9	0.06
Raker	3.4	1.6	0.11
Tramper	8.3	3.9	0.27

<sup>a</sup>Absorbed daily dosage assumes 7.1% dermal absorption, 50% respiratory uptake of tribufos as a vapor with occupational exposure, inhalation rate of 14 L/minute, body weight of 75.9 kg, and 8-hour workday; the value represents the geometric mean for handlers and the arithmetic mean for harvesters based on the distribution of the data.

<sup>b</sup>Seasonal average daily dosage assumes that workers are exposed 21 days in a 45-day season.

<sup>c</sup>Lifetime average daily dosage assumes an exposure over 40 years of a 70-year lifespan.

Source: CalEPA 2004

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**5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES**

Agricultural workers who use tribufos as a defoliant in cotton fields will have higher exposure to this substance than the general population. This includes personnel who mix or load tribufos for aerial or ground-based spraying, pilots, flaggers, or workers who tend to the cotton plants post application.

Comparison of the data presented in Tables 5-7 and 5-8 indicates that dermal and inhalation exposure to workers treating cotton fields with tribufos will be several orders of magnitude greater than the average daily dietary intakes of the general population. Also, field workers who tend to cotton plants are potentially exposed to high levels of tribufos from postapplication residues.

Children of agricultural employees who work with tribufos are potentially exposed to residues from their parent's work clothing. Researchers have studied organophosphate residues in vehicles and homes of agricultural workers in the state of Washington and determined that the transport of pesticides from the workplace to the residence on a worker's clothing or person could lead to exposure to family members (Curl et al. 2002; Loewenherz et al. 1997; Lu et al. 2000). Take-home exposures to family members can be reduced by changing out of work clothes and shoes before entering the home and laundering work clothes separately from other family clothing.