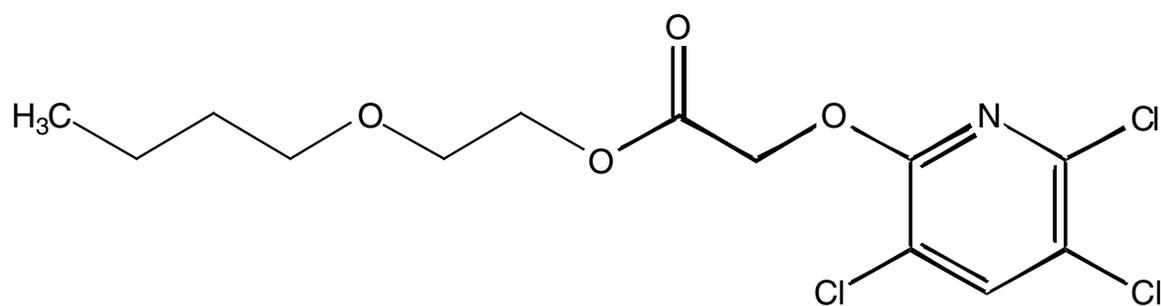


Chapter 4 — Triclopyr



4 Table of Contents — Triclopyr

4.1 INTRODUCTION	4-1
4.2 TRICLOPYR TOXICITY TO HUMANS AND LEVELS OF CONCERN	4-2
4.2.1 HEALTH EFFECTS.....	4-2
4.2.2 LEVELS OF CONCERN FOR HUMANS.....	4-2
4.2.3 ROUTES OF EXPOSURE	4-3
4.2.4 BIOMONITORING STUDIES.....	4-4
4.2.5 PESTICIDE ILLNESS REPORTS	4-6
4.3 TRICLOPYR TOXICITY TO ANIMALS AND PLANTS AND LEVELS OF CONCERN.....	4-7
4.3.1 MAMMALS.....	4-8
4.3.1.A Metabolism and Pharmacokinetics of Triclopyr.....	4-9
4.3.1.B Acute Toxicity of Triclopyr.....	4-10
4.3.1.C Sub-Chronic Toxicity of Triclopyr.....	4-12
4.3.1.D Chronic Toxicity and Carcinogenicity of Triclopyr.....	4-12
4.3.1.E Reproductive and Developmental Toxicity of Triclopyr.....	4-19
4.3.1.F Neurotoxicity.....	4-23
4.3.1.G Immunotoxicity	4-23
4.3.1.H Endocrine Disruption.....	4-24
4.3.1.I Effects on Mammalian Wildlife.....	4-24
4.3.1.J Levels of Concern for Mammals	4-24
4.3.2 OTHER TERRESTRIAL ORGANISMS.....	4-25
4.3.2.A Birds	4-25
4.3.2.B Terrestrial Invertebrates.....	4-26
4.3.2.C Terrestrial Plants	4-26
4.3.2.D Soil Microbes.....	4-28
4.3.3 AQUATIC ORGANISMS	4-28
4.3.3.A Fish.....	4-29
4.3.3.B Amphibians.....	4-32
4.3.3.C Aquatic Invertebrates.....	4-32
4.3.3.D Aquatic Plants.....	4-34
4.3.4 DATA GAPS.....	4-34
4.4 ENVIRONMENTAL FATE OF TRICLOPYR	4-38
4.4.1 OVERVIEW.....	4-38
4.4.2 WATER SOLUBILITY AND SOIL BINDING OF TRICLOPYR.....	4-39
4.4.3 PERSISTENCE OF TRICLOPYR.....	4-39
4.4.3.A Microbial Degradation.....	4-42
4.4.3.B Transport by Air.....	4-42
4.4.3.C Transport by Water.....	4-43
4.4.3.D Uptake by Plants.....	4-43
4.4.3.E Field Studies on the Environmental Fate of Triclopyr.....	4-44
4.4.4 GARLON 4 ULTRA PRODUCT PROFILE.....	4-46
4.5 EXPOSURE ASSESSMENT AND RISK CHARACTERIZATION FOR TRICLOPYR.....	4-46
4.5.1 CHEMICAL-SPECIFIC EXPOSURE PARAMETERS.....	4-47
4.5.2 APPLICATION METHODS FOR TRICLOPYR	4-50
4.5.3 WATER CONTAMINATION ESTIMATES	4-50
4.5.4 RISKS TO HUMANS.....	4-54
4.5.4.A Workers	4-54

4.5.4.B General Public 4-57

4.5.5 RISKS TO WILDLIFE 4-64

4.5.5.A Terrestrial Wildlife 4-64

4.5.5.B Terrestrial Plants 4-66

4.5.5.C Aquatic Wildlife 4-70

REFERENCES FOR CHAPTER 4..... 4-74

4.1 Introduction

Triclopyr is a pyridinecarboxylic acid herbicide that is selective for broadleaf plants and is not toxic to grasses and conifers. It is used for controlling unwanted woody plants, annual and perennial broadleaf weeds in forest, and on non-crop areas including industrial sites, rights-of-way (i.e., electrical power lines, communication lines, pipelines, roadsides, railroads), fence rows, non-irrigation ditch banks, and around farm buildings. Triclopyr kills plants by mimicking auxins—plant growth hormones. Triclopyr damages the plant by causing uncontrolled growth.

There are two forms of triclopyr currently registered for use in the US—the triethylamine (TEA) salt and the butoxyethyl ester (BEE). Triclopyr TEA was first registered in 1979 and triclopyr BEE was first registered in 1980. Although triclopyr has been registered almost as long as glyphosate, it is used much less extensively—one to three million pounds annually were estimated in 2001.¹ Triclopyr is not widely used in residential settings. In California, where more recent use data are available, use of triclopyr salts and esters has fluctuated around 160,000 ± 17,000 lbs per year from 1995 through 2006.² Triclopyr is currently registered for use in the European Union and was re-evaluated most recently in 2006.³

Garlon 4 Ultra, containing the active ingredient triclopyr BEE and a methylated seed oil adjuvant, was designated as a candidate herbicide for use by MMWD. Most toxicity studies available in the literature were done with Garlon 3 (containing triclopyr TEA salt as the active ingredient and ethanol, triethylamine and ethylene diamine tetraacetic acid (EDTA) as other ingredients) or Garlon 4 (containing triclopyr BEE and kerosene as an adjuvant).⁴ There are substantial differences in acute toxicity between the BEE and TEA derivatives, with BEE much more toxic in aquatic settings. The effect of changing the adjuvant from kerosene in Garlon 4 to methylated seed oil in Garlon 4 Ultra is unknown—there are no toxicity studies available for Garlon 4 Ultra. However, the toxicity of the two adjuvants alone is on the same order of magnitude: mammalian LC₅₀ for kerosene is 16,000–23,000 mg/kg⁵ and mammalian LC₅₀ for methylated seed oil has been determined to be greater than 2,000 up to 17,000 mg/kg, depending on the length of the fatty acid carbon chain.⁶ The USFS notes that the toxicity of kerosene to aquatic species is approximately 100–1,000 fold less than triclopyr BEE, with LC₅₀ values of 200–3,000 mg/L, which suggests that the acute aquatic toxicity of Garlon 4 is dominated by triclopyr BEE. Methylated seed oil adjuvants such as the one in Garlon 4 Ultra have low acute aquatic toxicity (53.1 mg/L for bluegill sunfish, *Lepomis macrochirus*⁷), similar to that for kerosene (9.5 mg/L for guppies, *Poecilia reticulata*⁸). Thus, we would not anticipate that a change in adjuvant would significantly alter the acute aquatic toxicity of the product, unless synergistic effects come into play. Changes in chronic toxicity are difficult to predict.

This chapter focuses on the human toxicity, ecotoxicity, and environmental fate of triclopyr, drawing from the United States Forest Service's Human Health and Ecological Risk Assessment of Triclopyr, 2003⁵ (USFS 2003), US EPA's Re-registration Decision 1998⁹ (RED 1998), EPA's pesticide tolerance decision in the Federal Register in 2002 (EPA 2002),¹⁰ and the EPA Ecotox database¹¹ (Terretox for the terrestrial database and AQUIRE for the aquatic database). The chapter focuses on the toxicity of triclopyr BEE, but the toxicity differences between triclopyr BEE and TEA to aquatic life are also discussed. An extensive survey of the peer-reviewed literature was conducted to find additional research results not available in these documents.

4.2 Triclopyr Toxicity to Humans and Levels of Concern

The active pesticide ingredient in Garlon 4 Ultra is triclopyr butoxyethyl ester (triclopyr BEE), which undergoes hydrolysis in the human body to form triclopyr acid. The triethylamine salt used in Garlon 3 A has a low acute toxicity similar to that of Garlon 4 Ultra, but differs in being substantially more irritating to the eyes and skin.

There are few data available on potential acute and chronic health effects from exposure to triclopyr. Most of the human studies available involve monitoring of a small number of male forestry workers exposed to triclopyr for three months or to less than a year. Most of the toxicity data used by US EPA for assessing risk to humans is from animal studies, which are summarized in Section 4.3.

Triclopyr is absorbed in humans through the skin, the most common route of exposure. Inhalation exposure to triclopyr is much lower than dermal exposure due to the low volatility of both triclopyr TEA and BEE.

There are no case reports of acute toxic effects of triclopyr exposure; nor are there any incidents reported in either TESS or SENSOR pesticide illness surveillance systems. The California Pesticide Incident Surveillance Program (PISP) reported 17 cases over a ten year period, all involving irritant effects to the eyes, skin, or upper respiratory system (Table 4-1). The most important immediate concern to workers is skin and eye irritation, which can be mitigated with protective clothing and good work practices.

There are no epidemiological studies of acute or potential chronic health effects related to triclopyr exposure. One of the biomonitoring studies discussed below which used a mathematical model to estimate absorbed dose of triclopyr found that some workers had exceeded the recommended EPA reference dose.

4.2.1 Health Effects

There are no case reports or epidemiological studies related to human triclopyr exposure. See Section 4.3.1 for animal data on chronic health effects.

4.2.2 Levels of Concern for Humans

For the MMWD risk assessment, we used the acute triclopyr RfDs for women of childbearing age (0.05 mg/kg-day) and for the general population (1 mg/kg-day). For the scenario of drinking water contaminated with long-term runoff, we used the chronic PAD of 0.012 mg/kg-day developed by EPA for the triclopyr degradation product TCP.

The acute EPA RfD of 1.0 mg/kg-day for triclopyr is based on a NOAEL for a developmental toxicity study in rats of 100 mg/kg-day, where unspecified “clinical signs” were observed on gestation day seven at the next highest dose of 300 mg/kg-day (see Section 4.2.1 below). This NOAEL was divided by both intra- and inter-species factors of 10 to give a value of 1.0 mg/kg-day for adult males. The acute RfD for women of child-bearing age is 0.05 mg/kg-day, based on a multi-generation reproductive toxicity study in rats. The NOAEL is 5 mg/kg-day, based on birth defects including exencephaly (brain outside the skull) and ablepharia (no eyelids) at the next higher dose of 25 mg/kg-day. The chronic EPA RfD is based on a NOAEL of 5 mg/kg-day

for parental/systemic toxicity in a two-generation study in rats based on the observation of proximal tubular degeneration of the kidneys of P1 and P2 parental rats at the next highest dose of 25 mg/kg/day, adjusted with both intra- and inter-species factors of 10 to give an RfD of 0.05 mg/kg-day. In EPA's 2002 tolerance notice for triclopyr, the chronic RfD is also applied to short- and intermediate-term exposure times of one to six months.¹⁰

Population adjusted doses (PADs) for TCP, the primary degradation product of triclopyr, were developed by US EPA in the 2002 re-evaluation of triclopyr tolerances.^{10, 12} The acute PAD for women of child-bearing age is 0.025 mg/kg-day, based on a NOAEL of 25 mg/kg-day for increased incidence of hydrocephaly and dilated ventricles in rabbits seen at the next higher dose of 100 mg/kg-day. The NOAEL was adjusted with the intra- and inter-species uncertainty factors of 10, as well as an additional Food Quality Protection Act (FQPA) factor of 10 to protect vulnerable populations. The chronic PAD is 0.012 mg/kg-day, based on a NOAEL of 12 mg/kg-day observed in a 1-year dog study in which alterations in clinical chemistry levels were observed at the next higher dose of 48 mg/kg-day. EPA adjusted the NOAEL with the intra- and inter-species uncertainty factors of 10, as well as an additional FQPA factor of 10 to protect vulnerable populations.

4.2.3 Routes of Exposure

Potential human exposure to triclopyr is through skin absorption, inhalation, ingestion, or the eye. Triclopyr BEE is of low acute toxicity to humans and is placed by the US Environmental Protection Agency (EPA) in Category III slightly toxic. The TEA salt is classified as Category I (highly toxic) because it is corrosive to the eyes in animal tests. The oral reference dose (RfD) determined by the EPA that is not likely to cause harmful effects during a lifetime for both adults and children is 0.05 mg/kg-day and the acute RfD is 1.0 mg/kg-day.⁹

Dermal: The skin is the major route of exposure for triclopyr, where it is slowly absorbed. In the only study in which triclopyr BEE was applied to the skin of humans it continued to be excreted in the urine in decreasing amounts for four days.¹³

In a study of five male human volunteers, 0.65-1.10 mL of undiluted Garlon 4 (equivalent to 5.0 mg/kg body weight of triclopyr BEE) was applied to the left forearm (mean 259 mg), and wiped off with a paper towel after eight hours.¹³ Blood was drawn 11 times from 0.5 hour to 72 hours after the application, and urine was collected over the next 96 hours. Triclopyr was detected in the blood at three hours after application. Peak blood levels were found at 12 hours, and triclopyr was undetectable at 72 hours. The highest blood level found in any individual was 0.08 µg/mL. An average of 1.37 percent of the applied dose was excreted in the urine. Absorption through the skin was slow with a half-time of 16 hours. The largest amount excreted in the urine occurred in the first 12-24 hour period (0.56-2.5 mg) and declined to a measurable but low level by 84-96 hours. The authors fit the data to a one-compartment pharmacokinetic model which corrected for the 81.7 percent recovery found after oral administration, and concluded that an average of 1.65 percent of the dermal dose was absorbed.

In a study comparing rat and human skin absorption of xenobiotics, 1.7 cm diameter full thickness samples of rat skin and normal human female breast skin obtained from surgery were placed in diffusion cells and allowed to equilibrate for about 30 minutes.¹⁴ Skin tissue in 'flow-

through' diffusion cells closely resembles the true skin barrier because of the continuous flow of a receptor fluid across the underside of the skin which mimics dermal blood flow, and maintains skin viability. Carbon-14-labeled triclopyr BEE (> 99 percent pure) was applied to the skin in the amount of 15.0 mg/cm² and then occluded or left open to the atmosphere. Receptor fluid was collected for up to 72 hr, scintillation fluid was added, and levels of ¹⁴C radioactivity remaining in the skin determined.

The absorption capacity through un-occluded human skin for triclopyr BEE was much less than for the rat. The recovery of radioactivity at 72 hours was 5.1 percent in human skin versus 63 percent in rat skin, that is, 12 times more triclopyr BEE penetrated the skin of the rat. A much larger amount was left on the surface of human skin (48.4 percent) than on rat skin (12.3 percent), and recovered in the diffusion cells of human skin (41.1 percent) versus rat cells (8.6 percent), both of which indicate greater absorption in the rat.

The skin is known to contain significant xenobiotic-metabolizing activity, and some degree of metabolic conversion of topically applied compounds will occur during percutaneous absorption. Such cutaneous metabolic events may be an important determinant of systemic exposure, and since the skin contains considerable esterase activity, it is likely that the ester, triclopyr BEE, may undergo a degree of hydrolysis during absorption, resulting in the formation of triclopyr acid. Triclopyr TEA will also rapidly dissociate to form triclopyr acid.

Inhalation: Triclopyr acid has a low vapor pressure of $<1 \times 10^{-8}$ mm Hg (25°C), and triclopyr BEE has a moderately low vapor pressure of 3.6×10^{-6} mm Hg (25°C). Potential exposure via this route is low as discussed in the biomonitoring studies below. No Occupational Health and Safety Administration (OSHA) permissible exposure limit (PEL) or ACGIH threshold limit value (TLV) in air have been set for triclopyr.

Ingestion: Orally administered triclopyr is rapidly absorbed and excreted, with most excreted unchanged in the urine. Six male volunteers were administered an oral dose of 0.1 mg/kg body weight (one tenth the adult male, acute RfD) as a solution of 0.098 mg triclopyr per mL of apple juice. Three weeks later a higher oral dose of 0.5 mg/kg body weight (half the adult male acute RfD) was administered at 0.176 mg/mL. Blood was drawn at 0.5, 1, 2, 3, 4, 6, 8, 12, 24 and 48 hours after dosing. Urine was collected 13 hours prior to dosing, 0-6 and 6-12 hours post dosing, and then every 12-hour period for the next 60 hours.

Triclopyr was detected in the blood at 0.5 hours at both dose levels. Peak blood levels at two hours were 0.27 µg/mL at the lower dose and 1.44 µg/mL at the higher dose. Triclopyr was not detected in the blood 24 hours after the lower dose and 48 hours after the higher dose. Most of the triclopyr was excreted unchanged in the urine (81.7 percent). The potential major metabolite of triclopyr—3,5,6-trichloropyridinol—was less than 0.5 percent of the total dose in pooled 24 hour urine samples from the higher dose study. This suggests that very little triclopyr is metabolized in humans.¹³

4.2.4 Biomonitoring Studies

There are four biomonitoring studies of forest workers applying triclopyr, involving a total of 26 forest workers over a period of two to ten days, and another of three roadside spray workers

followed for three seasons. The workers were all volunteers and were monitored as part of their usual work day. All of the workers' urine was collected for the duration of the study. Triclopyr was excreted unchanged in the urine at low to non-detectable amounts in the part per billion (ppb) range from both inhalation and dermal exposure.

In general, the estimated absorbed dose was lower in backpack sprayers than boom type sprayers, depending on foliage contact (whether working with stumps or trees, and the height of the trees). There was great variability among individual workers depending on the use of protective clothing, gloves and work habits.

In an inhalation study measuring triclopyr BEE, absorption was very low, accounting for less than two percent of the estimated daily absorbed dose compared to the estimate of 98 percent from dermal absorption.

The amounts found in the urine are a measure of recent exposure at the time of sampling and cannot be used to ascertain or predict past or future exposures over time. Testing biological samples for triclopyr is not available in standard medical care facilities or laboratories.

2001: The urine of forestry workers applying Garlon 4 in Quebec, Canada was monitored on the final day of a five-day work week.¹⁵ Eight workers were applying dilute Garlon 4 (20 percent Garlon 4 and 80 percent mineral oil) with a backpack unit directly on the stumps of recently cut trees, and two workers were applying dilute Garlon 4 (12.6 liters of Garlon 4 mixed in 1,800 liters of water) under high voltage transmission lines from a tractor-mounted boom.

The workers collected all their urine from the start of their workday until the first urination the following morning. The average amount of triclopyr found in urine was 0.0564 mg/kg of body weight—from 1.04 to 12.98 mg/day in the eight backpack sprayers, and 3.61 to 5.97 mg/day in the two boom sprayers. A mathematical model was developed to estimate the absorbed dose from triclopyr exposure using the amount excreted in the urine by each worker. The mean estimated daily absorbed dose based on a simulated fraction recovered in the urine was 11.92 mg (34.9%) in the backpack sprayers and 14.4 mg (31.4%) in the boom sprayers.

This dose would result in a cumulative urinary excretion of triclopyr equal to 1.45 mg/kg b.w. for a 24 h collection, 2.63 mg/kg b.w. for a 48 h collection and 2.83 mg/kg b.w. for a 72 h collection. Comparisons between the estimated daily doses absorbed by the workers in this study and the RfD show that there is a potential health risk for these workers under the current conditions. Since there is no observed effect in humans exposed to triclopyr, there is no proof that the NOEL established for rats corresponds to a safe dose for humans. One worker was above the RfD.

1995: A two day biomonitoring study of skin and inhalation exposure to Garlon 4 was conducted in California in 1995 of ten forestry workers applying Garlon 4 (containing 61.6% (5.56 lb/gal) of the formulated product) using backpack sprayers and spray wands.¹⁶ Twenty-four-hour urine samples were collected to estimate absorbed dose.

Dermal exposure was monitored by measuring residues on work clothing worn next to the skin (long sleeved cotton T-shirts and knee-length socks) and wipe samples of the hand, face, and neck. Upper body exposure accounted for 45 percent of exposure, legs 33 percent, hands 19 percent and face/neck three percent. Mean measured dermal triclopyr exposure of 18.67 mg per person accounted for 98 percent of the estimated daily absorbed dose for the two days.

Triclopyr has a low vapor pressure (0.2 mPa at 25 °C), and inhalation is not a major route of exposure. Comparing the inhalation exposures reported below to the worker exposures reported above shows that inhalation accounts for approximately 0.3-5% of a workers' measured dose. Inhalation doses of triclopyr BEE measured using personal air monitors ranged from 32.6 to 71.7 µg per day, accounting for 1.89 percent of the mean daily absorbed dose for the two days. Although air concentrations of triclopyr are below the human RfD, triclopyr air concentrations may still damage plants.

Twenty-four hour urine samples were collected to obtain an estimate of absorbed dose (EAD). Overall EAD from urinary triclopyr (0.058 mg/kg bw) was significantly greater than that estimated from dermal plus inhalation monitoring (0.013 mg/kg bw) $p < 0.01$, suggesting that the methodology used to assess exposure did not provide a comprehensive assessment.

1990-1993: Urine and air monitoring data were collected on three workers applying triclopyr to Louisiana roadways at an application rate of 0.84 acid equivalents per hectare over four spray seasons from 1990 to 1993.¹⁷ The amount of triclopyr detected in urine per day ranged from non-detectable to 438 µg, and in breathing space air from 2 to 35 µg.

1990: A study was conducted in sixteen forestry worker volunteers at three different sites applying Garlon 4 using backpack sprayers and hand guns. Four to six pounds (1.82 to 2.72 kg) of triclopyr were applied per day.

Dermal exposure was monitored by applying body surface patches and use of hand rinses. Inhalation exposure was monitored by personal air concentration in the breathing zone. All urine was collected over a five-day period—the day before, the day of, and three days after application—to obtain the amount of triclopyr excreted in order to estimate absorbed dose.

The mean exposure rate was 0.004 (0.00035–0.01428) mg/kg per lb a.e. handled. Neither of two workers with the highest exposure rates (0.01428 and 0.01176) wore gloves. The mean exposure rate of 0.00221 (0.0015–0.00506) mg/kg per lb a.e. was much lower when including only the fourteen workers who wore gloves. The mean dermal absorption rate was 0.046 mg/hour (0.0163–0.0873). Personal air levels ranged from 5 to 15 µg/m³.^{18, 19}

4.2.5 Pesticide Illness Reports

The California PISP reported 17 cases of triclopyr-related pesticide incidents in ten years as shown in Table 4-1. All were local irritant effects and there were no cases of systemic poisoning. The most important immediate concern to workers is skin and eye irritation, which can be mitigated with protective clothing and good work practices; long-term effects of human exposure to triclopyr are not known. There are no incidents involving triclopyr in either TESS or SENSOR pesticide surveillance systems.

Table 4-1: Triclopyr-related Illnesses Reported by California Physicians to the Pesticide Incident Surveillance Program (PISP) 1987 to 2004

Year	Respiratory		Skin/Eye		Total
	Definite/Probable	Possible	Definite/Probable	Possible	
2004	2	1	-	-	3
2003	-	3	-	-	3
1999	-	-	1	-	1
1997	-	2	-	-	2
1996	1	-	-	-	1
1992	-	-	1	1	2
1991	-	-	1	-	1
1989	-	-	1	-	1
1988	-	-	1	-	1
1987	-	-	2	-	2

Data source: CA DPR Pesticide Illness Surveillance Program, reference 20.

4.3 Triclopyr Toxicity to Animals and Plants and Levels of Concern

This section of the report summarizes triclopyr toxicity to nine taxa groups, including mammals, birds, fish, amphibians, terrestrial and aquatic invertebrates, terrestrial and aquatic plants, and soil microorganisms. Although triclopyr has been registered in the US since 1979, there are still very few studies on triclopyr that are not part of the EPA registration process.

The acute oral, dermal and inhalation toxicity in mammals of triclopyr acid, TEA and BEE is low. Triclopyr BEE is rated as Category III (slightly toxic) and the TEA salt is Category I (highly toxic for eye irritation) for mammals. The toxicity of triclopyr BEE to aquatic organisms is high compared to glyphosate. Triclopyr toxicity to wildlife ranges from not acutely toxic to slightly acutely toxic for birds and honeybees, and slightly to highly acutely toxic in fish, amphibians and aquatic invertebrates. Aquatic toxicity depends strongly on the triclopyr formulation—triclopyr BEE is more toxic to aquatic organisms than triclopyr acid or TEA salt. Triclopyr's effects on soil microorganisms are not well-defined.

The toxicity information used in this section comes from the United States Forest Service's Human Health and Ecological Risk Assessment 2003⁵ (USFS 2003), EPA's Re-registration Decision 1998⁹ (RED 1998), and the EPA EcoTox database ("Terretox" for the terrestrial database and "AQUIRE" for the aquatic database).

Levels of concern for triclopyr are also summarized in this section, with Table 4-8 on page 4-35 presenting the toxicity reference values (TRVs) selected for the MMWD risk assessment and the USFS TRVs for comparison.

For wildlife, we primarily used the same TRVs as the USFS, adjusting the value downward when additional data were available indicating toxicity at concentrations below the USFS TRV, or when only LC₅₀ values were available instead of NOECs. This approach used EPA methodology for assessing effects on endangered species.²¹ The adjustment employed was to

divide the LC₅₀ by six (or 20 in the case of salmonids), based on an extensive review of existing ecotoxicological data on pesticides.²² The review found that sublethal effects did not typically occur at concentrations below one-fourth to one-sixth of the LD₅₀, when taking into account the same percentages or numbers affected, test system, duration, species, and other factors. This effect is termed the “6x hypothesis.” However, it should be noted that this review is almost 30 years out-of-date, and that the factor of six is meant to translate an LC₅₀ to a NOEC *of the same species*. The use of a single NOEC for all species in a taxa group suggests that interspecies variability may not be fully accounted for by the factor of six. Further, the factor of six appears to be too low for salmonids. As discussed in the EPA report, salmonids’ olfactory ability seems to be particularly sensitive to pesticide concentrations 20 times lower than the LC₅₀.²³ Thus, for fish we divide LC₅₀ values by 20 to obtain the TRV used in the MMWD risk assessment.

Toxicity reference values for both triclopyr BEE and triclopyr TEA are discussed. Both chemicals are under consideration for use in the MMWD watershed. For long-term runoff where several months might pass before a rainstorm with sufficient volume to cause runoff occurs, TRVs for the triclopyr degradation product 3,5,6-trichloro-2-pyridinol (TCP) are used. This is appropriate, since both triclopyr TEA and triclopyr BEE are transformed relatively rapidly in the environment to triclopyr acid, which degrades primarily to TCP. At 54 days after application, 88% of triclopyr acid was converted to TCP.⁹⁶

4.3.1 Mammals

Most of the data on toxicity of triclopyr to mammals is from studies in laboratory animals for support of registration of the herbicide with the EPA. There are very few studies of triclopyr available in the open literature, and the discussion below is based on unpublished studies summarized in the EPA RED⁹ and the USDA Forest Service review.⁵ Results of studies of laboratory animals are summarized in Tables 4-2 to 4-6. The EPA considers triclopyr acid (3,5,6-trichloro-2-pyridinyloxyacetic acid) and its triethylamine salt (TEA) and butoxyethyl ester (BEE) as bioequivalent in toxicity to mammals.

Triclopyr is poorly absorbed through the skin and has low acute oral, dermal and inhalation toxicity. It can be a mild to severe eye and skin irritant depending on the formulation. The studies on sensitization (allergic dermatitis) are ambiguous. Triclopyr causes severe birth defects in rats at relatively low levels of exposure (NOEL = 5 mg/kg-day), and the US EPA reference dose for triclopyr of 0.05 mg/kg-day for women of childbearing age is based on this effect. Adverse liver and kidney effects and hematological changes have also been noted in animal studies. The triclopyr degradation product TCP is a developmental toxicant with a NOAEL of 25 mg/kg-day and causes changes in blood chemistry in chronic exposure studies.

The EPA classified triclopyr as Group D (Not Classifiable as to Human Carcinogenicity) in 1998 based on a consensus recommendation of the agency's Carcinogenicity Peer Review Committee (CPRC). The CPRC's review found the animal evidence to be marginal (not entirely negative, but yet not convincing) and not supported by additional data from structural analogs or genotoxicity data. This decision was in contradiction to the 1986 EPA guidelines requiring a compound to be classified as a carcinogen if it caused cancer in two species of laboratory animals. The latest revised guidelines are more lenient, allowing the EPA to exercise considerable judgment based on the nature and quality of the data.

There are much more data on reproductive effects of triclopyr, several of which found adverse maternal and development outcomes, including fetal malformations (see Table 4-6). Maternal toxicity was high, and the most severe adverse outcomes were found at the highest dose tested (HDT). A study of the reproductive and developmental effects of TCP, the major metabolite of triclopyr, found adverse effects on fetal development, but only at dose levels that also produced maternal toxicity.

4.3.1.A Metabolism and Pharmacokinetics of Triclopyr

Triclopyr is poorly absorbed and rapidly excreted unchanged in the urine following oral and dermal administration. In rats fed 3 or 60 mg/kg of ¹⁴C-triclopyr acid, approximately 89 to 95 percent of unchanged triclopyr was recovered in the urine; very little residue was found in the feces or carcass. The half-time for oral absorption was 3.61 hours and for urinary excretion of unabsorbed triclopyr was 1.1 hours.²⁴ In rabbits administered a dermal dose of 0.5 to 2.1 mL of 50 percent Garlon 4E (diluted with water) applied five days a week for three weeks, average recovery of triclopyr in the urine was 8 to 9 percent of the applied dose (see sub-chronic section for further results of these studies)²⁵ In another study in rabbits, 1.5 percent of a 2 g/kg dose of triclopyr acid was absorbed through the skin.²⁶

A lactating Holstein cow fed 454.4 mg of triclopyr in grain over a four-day period excreted 86.4 percent unchanged in the urine. No residues were found in the milk or feces.²⁷

The pharmacokinetics of triclopyr is very different in the dog, which is unique in its limited capacity to clear weak acids from the blood and excrete them in the urine.²⁴ The Dow Chemical Company (manufacturer of triclopyr) was critical of the EPA's characterization of decreased kidney excretion of the red dye phenolsulfophthalein (PSP) in dogs as a toxic effect and using it as a basis for setting an acceptable level of exposure for triclopyr. Studies conducted by the company showed that PSP is competing with triclopyr for excretion in dogs, an effect that was not present in the monkey or the rat even at much higher doses.^{28, 29} The EPA reclassified decreased PSP excretion in dogs as a physiological response and not an adverse effect.³⁰ Other effects on the kidney were reflected by changes in clinical chemistry (blood urea nitrogen (BUN) and creatinine) are classified as adverse effects and are discussed further in the sub-chronic section.

TCP metabolite: The major metabolite of triclopyr in mammals is 3,5,6-trichloro-2-pyridinol (TCP) which is also the major metabolite of the organophosphate insecticide chlorpyrifos (Dursban, Lorsban). The organothiophosphate structure found in chlorpyrifos is not present in either TCP or triclopyr, and neither are cholinesterase inhibitors. EPA derived a provisional acute Population Adjusted Dose (PAD) of 0.025 mg TCP/kg-day based on NOAEL of 25 mg/kg-day from a developmental toxicity study in rabbits, in which increased incidence of hydrocephaly and dilated ventricles in rabbits was seen at the next higher dose of 100 mg/kg-day. An uncertainty factor of 1,000 was used to obtain the PAD. The chronic PAD of 0.012 mg TCP/kg-day is based on data from a chronic study in dogs using an uncertainty factor of 1,000.¹⁰ Changes in clinical chemistry were found at a LOAEL of 48 mg/kg-day, but no effects at a NOAEL of 12 mg/kg-day. EPA has assessed the combined likely exposures to TCP from both triclopyr and chlorpyrifos using very high exposure assumptions, and found no risks of concern.

TCP was not considered fetotoxic or teratogenic in either rats or rabbits, except at dose levels that produced maternal toxicity.³¹

Other ingredients: Garlon 4 Ultra contains 39.55% by weight of a non-petroleum, methylated seed oil solvent with lower toxicity than kerosene used in Garlon 4 formulations. Methylated seed oils are products of the reaction of plant oils such as soy and canola with methanol or ethanol and are generally characterized as not acutely hazardous.³² Little is known about their sub-chronic toxicity, but it is not likely to be high (see Chapter 9). Low molecular weight methylated seed oils are approved as food additives and are classified by EPA as List 4B minimal risk inert. The product label does not specify the molecular weight of the methylated seed oils in Garlon 4 Ultra.

Garlon 3 contains 55.6% by weight of a mixture of ethanol (~1%),⁵ triethylamine and ethylenediamine tetraacetic acid (EDTA) as other ingredients. The acute toxicity of ethanol to mammals is low, although drinking sufficient quantities of alcoholic beverages is associated with cancer, birth defects, and reduced fertility in males. Nevertheless, any potential human exposures to ethanol resulting from use of Garlon 3 are likely to be insignificant relative to exposures from ingestion of alcoholic beverages or fermented fruits and vegetables. Triethylamine is moderately acutely toxic by inhalation. The chelating agent EDTA has low acute toxicity and is frequently used in many drug preparations, cosmetics and other personal care products, and is approved for use in foods by the US Food and Drug Administration (FDA).

4.3.1.B Acute Toxicity of Triclopyr

The acute oral, dermal and inhalation toxicity in mammals of triclopyr acid, TEA and BEE is low (see Table 4-2). Products containing triclopyr may cause irritation to the skin and eyes, with technical grade triclopyr acid (technical) being a slight irritant, while triclopyr BEE causes more severe skin reactions, most likely due to more rapid absorption. Triclopyr TEA is not a primary skin irritant, but is more irritating via ocular exposure. Both TEA and BEE have been found to be sensitizers, causing allergic contact dermatitis (delayed hypersensitivity) in some studies but not others. Inhalation is not a major route of exposure to triclopyr.

Table 4-2: Acute Toxicity of Triclopyr in Experimental Animals

Mode	Formulation	Oral, Dermal LD ₅₀ (mg/kg) Inhalation LC ₅₀ (mg/L)	EPA Toxicity Category
Rat oral ³³	Technical grade	1,915 M >2000 <5050 F	III
Rat oral ⁹	Technical grade	>2000 M/F	III
Rat oral ³⁴	TEA (44.4% a.i.)	594 M, 828 F	III
Rat oral ⁵	BEE	803 M,F	III
Rat dermal ³⁵	Free acid	729 M, 630 F	III
Rabbit dermal ³⁶	Free acid or BEE	>2,000	III
Rabbit dermal ³⁷	TEA (46.5%)	> 5,000	IV
Rabbit dermal ³⁸	Technical grade	> 5,050	IV
Rat inhalation ³⁹	TEA (44.4% a.i.)	> 2.6 M/F	IV
Rat inhalation ⁴⁰	BEE (97.1% a.i.)	> 4.8 M/F	IV

Dermal Exposure: Triclopyr is poorly absorbed through the skin, which is reflected in high dermal LD₅₀ values ranging from 2,000 to >5,050 mg/kg as shown in Table 4-3. Both contact and allergic dermatitis from exposure to triclopyr have been studied in rabbits and guinea pigs. Triclopyr BEE causes more severe skin irritation than triclopyr acid or TEA, which may be due

to more rapid absorption. Triclopyr TEA is not a primary skin irritant, but allergic contact sensitization was found in some studies, but not others.

Table 4-3: Dermal Toxicity of Triclopyr to Mammals

Test animal	Study Duration	Doses Tested (mg/kg-day)	Observed effects
Rabbits 6 M/F ⁴¹	4 hrs	500 mg tech. covered intact skin	Slight irritation
Rabbit 5M/5 F ³⁸	21 days	5,050 mg tech. intact skin	Erythema in 4 of 10 animals
Guinea pig 10 M/F ⁴²	24 hours	400 mg tech. to intact skin	Not a sensitizer, no changes.
Guinea pig 10 M ⁴³		Garlon 3A TEA undiluted	A sensitizer. Slight erythema in 4/10 animals.
Guinea pig 10 M ⁴⁴		Garlon 3A50% TEA	Not a sensitizer, no changes.
Guinea pig 10 M ⁴⁵		Garlon 3A 30% TEA	Not a sensitizer, no changes.
Guinea pig 10 M ⁴⁶		Garlon 3A 15% TEA	Slight erythema in 3/10, 4/10, 1/10, and 2/10 animals.
Guinea pig 40 M ⁴⁷		Garlon 3A (TEA) 0.4 ml + 4 dose levels ethyl pyridine	Slight erythema in 4/10, 3/10, 3/10, 1/10. Sensitization unrelated to ethyl pyridine contaminant
Guinea pig 40 M ⁴⁷		Garlon 4 (BEE) 0.4 ml + 4 dose levels ethyl pyridine	Sensitization unrelated to ethyl pyridine contaminant.
Guinea pig 10 M ⁴⁸ Rat 5M 5F ⁴⁹	1 day	Pathfinder II, 13.9% a.i (BEE) 7.5%, 2.5% to shaved backs.	Not a sensitizer. No mortality or treatment related gross pathology.

Ocular exposure: There are three studies of ocular toxicity of triclopyr, all in rabbits, in which 0.1 ml by volume was applied to the conjunctival sac of one eye for 24 hours, washed out with deionized water for one minute and followed up for seven days. Triclopyr TEA was found to be corrosive,⁵⁰ triclopyr acid a mild irritant,⁵¹ and triclopyr BEE a minimal irritant.⁵²

Inhalation exposure: The vapor pressure of triclopyr acid is very low ($< 1 \times 10^{-8}$ mm Hg at 25°C) and that of triclopyr BEE is moderately low (3.6×10^{-6} mm Hg at 25°C), which is reflected in the high inhalation LC₅₀ consistent with low acute inhalation toxicity (see Table 4-2). There are three studies of the inhalation toxicity of triclopyr, all in rats. Two of the studies were to determine the inhalation LC₅₀ of triclopyr TEA²⁰ and BEE.⁴⁰ In a study of ten Sprague-Dawley rats exposed to undiluted triclopyr technical fine powder at 2.5 mg/L, all exhibited decreased activity and piloerection. Body weight changes and abnormal necropsy findings of spotted lungs were found in one animal. This is the study on which EPA based its conclusion that inhalation exposure was not of toxicological concern.⁹ More study is needed to confirm this conclusion.

Intravenous exposure: In the only intravenous study available, triclopyr BEE was administered to male and female black Bengal goats at 2.97, 5.94, and 11.88 mg/kg body weight.⁵³ There were no signs of toxicity at the two lower doses; at the HDT, signs of toxicity included depression (as measured by sluggishness and unresponsiveness) and drowsiness after 10 minutes, miosis and fixation of the eyelid, increased secretion of nasal discharge and salivation, irregular skin itching, muscle tremors mainly on the posterior portion of the body, slight increase of body temperature, and increased frequency of defecation until four and one-half hours after administration.

4.3.1.C Sub-Chronic Toxicity of Triclopyr

There is testing of more species for the sub-chronic toxicity studies of triclopyr than for any chemical discussed in this report, with data reported in the rat, mouse, rabbit, horse, monkey, and cow. The studies are summarized in Table 4-4 below.

The most common adverse effects were in the kidney, found in all species tested. Increased kidney weight was found in the rat and mouse, proximal tubule degeneration in the rat, decreased excretion of the red dye PSP (phenolsulfophthalein) in the rat, dog and monkey, increased urinary protein in the mouse, increased blood urea nitrogen (BUN) in the mouse and horse, and increased creatinine in the dog and monkey. Abnormal changes on necropsy were found in the rat, mouse and rabbit. Hepatic effects were the next most frequently found. Increased liver weight was found in the rat, increased liver enzyme levels (transaminases AST/SGOT, ALT/SGPT) in the rat, mouse and dog, and liver cell (hepatocyte) histopathological changes in the rat, mouse, and horse. Hematological changes (hematocrit, hemoglobin, red blood cell count) were found in one study in rats and one in dogs. Non-specific effects such as decreased body weight and food consumption were also found.

In a study of beagle dogs that was the basis of the 2.5 mg/kg-day NOEL for triclopyr, BUN levels were unaffected, but another study found a statistically significant 57 percent increase in BUN.⁶⁴ The EPA reclassified the 2.5 mg/kg-day as an adverse effect, and set the NOEL for effects on the kidney at the next lower dose of 0.5 mg/kg-day. This lowered the provisional chronic RfD to 0.005 mg/kg. In a 1995 study in dogs, the NOEL based on renal histological changes was set at 5 mg/kg/day, and the LOEL at 20 mg/kg/day.⁵⁴

The EPA determined that risk assessments for short and intermediate term exposure were not required since the NOEL was > 1,000 mg/kg/day in a 21-day dermal toxicity study in rabbits.⁵⁵

A large mammal study of six adult Shetland pony geldings found no adverse effects at the lowest dose tested (60 mg/kg), but very significant adverse effects at 300 mg/kg, with two out of six ponies dying as a result of the exposure. This study suggests that larger mammals may be more sensitive to triclopyr than smaller ones. The author concluded that acute poisoning from proper use of the herbicide was unlikely.⁶⁵

4.3.1.D Chronic Toxicity and Carcinogenicity of Triclopyr

The EPA reports no increased cancer incidence associated with triclopyr exposure based on two available carcinogenicity studies, even though statistically significant increases in adrenal gland tumors (pheochromocytoma) were found in male rats and significant dose related increases in mammary gland adenocarcinoma were found in female rats and mice (see Table 4-5). There is an unpublished review of the cancer bioassay data on triclopyr submitted to EPA in support of its registration.⁵⁶ Having access to the unpublished documents, the USFS provided an analysis of the data and disputes about the accuracy of the cancer rating in the triclopyr risk assessment, quoted verbatim below:⁵

3.1.10. Carcinogenicity and Mutagenicity. *Information regarding the mutagenicity and carcinogenicity of triclopyr has been reviewed in detail by U.S. EPA (U.S. EPA/OPP 1998a,b,c) as well as in the open literature (Cox 2000). A review of the cancer bioassay data on triclopyr as also been submitted to U.S. EPA in support of the registration of this compound (Goodman and Hildebrandt 1996).*

Standard bioassays for carcinogenicity have been conducted in both rats (Eisenbrandt et al. 1987) and mice (Tsuda et al. 1987). Both of these studies are detailed in Appendix 5. In male rats and mice, no statistically significant dose-related trends in tumor incidence were apparent. Based on pair-wise comparisons (i.e., control group vs an exposed group), statistically significant increases were observed for some tumor types – benign and/or malignant pheochromocytomas combined as well as skin fibromas – in rats but not mice. In female rats and mice, there was a statistically significant dose-related increase in mammary gland adenocarcinomas.

The U.S. EPA/OPP (1998a) has reviewed these studies and determined that the evidence for carcinogenicity is marginal. This position is articulated briefly in the U.S. EPA/OPP (1998a) and, because of the importance of this decision to the risk assessment, the position is worth quoting directly:

“As a result of the August 9, 1995 meeting of the Agency's Carcinogenicity Peer Review Committee (CPRC), triclopyr was classified as a Group D chemical (not classifiable as to human carcinogenicity). This decision was based on increases in mammary tumors in both the female rat and mouse, and adrenal pheochromocytomas in the male rat, which the majority of the CPRC believed to be only marginal. Overall the majority of the CPRC felt that the animal evidence was marginal (not entirely negative, but yet not convincing). Therefore, the consensus of the CPRC was to classify triclopyr as a Group D chemical, based on what was considered only marginal response and the absence of additional support from structural analogs or genotoxicity. – U.S. EPA/OPP (1998a, p. 18).”

A detailed summary of the mutagenicity studies on triclopyr, most of which are negative, is detailed in Appendix 7.

The discussion of the potential carcinogenicity of triclopyr by Goodman and Hildebrandt (1996) is much more detailed and focuses on a re-evaluation of slides from the original studies as well as an assessment of tumor rates in historical controls. Both types of analyses are common and appropriate in the assessment of carcinogenicity data. Based on these analyses, Goodman and Hildebrandt (1996) assert that the triclopyr should not be classified as a carcinogen. In terms of the current risk assessment, this position has no impact: The decision by EPA/OPP (1998a) to classify triclopyr as Group D is accompanied automatically by a decision not to derive a cancer potency factor for triclopyr and hence, in terms of a risk assessment, the potential carcinogenicity of triclopyr is not considered quantitatively.

Cox (2000) has suggested that since triclopyr has been shown to cause a statistically significant dose-related increase in mammary gland tumors in both mice and rats, the U.S. EPA guidelines for cancer risk assessment indicate that triclopyr should be classified as a carcinogen. Cox (2000) cites the 1984 guidelines issues by U.S. EPA – i.e., FR 49: 46299-46300. The Agency has since issued additional draft guidelines in both 1996 and 1999, which are available at <http://cfpub.epa.gov/ncea/raf/cancer.cfm>. The 1984 guidelines do clearly indicate that a compound will be classified as a carcinogen if it has been shown to cause cancer in two species of laboratory animals. The more recent guidelines, however, are less proscriptive and allow the Agency to exercise substantial judgment based on the nature and quality of the data.

Notwithstanding the evolution of the U.S. EPA guidelines for cancer risk assessment, the basic point raised by Cox (2000) is well taken and is the substantial concern to the current risk assessment. Triclopyr has been shown to cause the same type of tumors in two species. In addition, while all cancers are a public health concern, the particular tumor type noted in rats and mice (breast cancer) is a common and important form of cancer in humans. Nonetheless, it is worth noting that none of the dose groups in either rats or mice evidenced a statistically significant pair-wise increase in breast tumors. In other words, the magnitude of the response was not substantial. The other important factor discussed by U.S. EPA/OPP (1998a) is the apparent lack of mutagenic activity of triclopyr. As detailed in U.S. EPA/OPP (1998a), only one study – a dominant lethal assay detailed in Appendix 7 – indicated any form of mutagenic activity and the other standard assays for genotoxicity were negative. This is an important point because even if the U.S. EPA had decided to classify triclopyr as a carcinogen, it is plausible that a threshold dose-response assessment would be conducted. In the current risk assessment, a threshold based approach is used for standard toxicity and this approach is based on the most sensitive endpoint – effects on the kidney (Section 3.4).

The only other potentially relevant information encountered in the literature is the epidemiologic report by Gambini et al. (1997). This study analyzes a cohort of rice farmers in Northern Italy, examining mortality patterns. The study attempts to determine whether excess risks for cancer could be detected and associated with chemical exposure. The study finds a significantly lower than expected number of deaths, with a slightly decreased overall cancer mortality. The study indicates that in 1990, 210 kg of triclopyr was used in the region of Italy in which the cohort of rice farmers lived.

This does not entirely alleviate concern for the potential carcinogenic activity of triclopyr. Based on a review of Eisenbrandt et al. (1987) and Tsuda et al. (1987) as well as the discussions in EPA/OPP (1998a) and Goodman and Hildebrandt (1996), there is no basis for asserting that these studies were seriously flawed.

Table 4-4: Sub-chronic Toxicity of Triclopyr to Mammals

Test animal	Study Duration (days)	Doses Tested (mg/kg-day)	Dose (endpoint) (mg/kg-day)	Observed effects
Rat Fischer 344 M/F ⁵⁷	91	0, 5, 20, 50, 250 technical (98% a.i.) in diet	5 (NOEL) 20 (LOEL)	Degeneration of kidney proximal tubules at 20 mg in males and females. Kidney wt increase in males at 50 mg in females at 250 mg. At HDT in males and females decreased activity, diarrhea, hunched posture, polyuria, facial swelling, stained walking on tiptoe (not found in survivors at day 6, decreased weight gain. GI tract, lung, liver, heart, kidney abnormalities at necropsy.
Rat Fisher 344 weanlings M/F ⁵⁸ 9 per sex per dose	91	0, 7, 28, 70, 350 BEE in diet	28, M (LOEL) < 7 F (LOEL)	In males at HDT, decreased body weight and hematologic changes. In males at 28 and 20 mg increased kidney and liver weight. In females at 7 mg hematologic changes and increase in liver and kidney weight. Histopathological changes in the liver (hepatocellular hypertrophy with eosinophilia, necrosis) in males at > 70 mg and in females at HDT. Histopathological changes in the kidney (degeneration/regeneration of the descending proximal tubules) in males at 70 mg and in F at HDT and increased ALP, ALT and AST.
Rat Wistar M/F 25 each ⁵⁹	21	24,240,480 dosed 5 days/week Garlon 4 dermal	24 (LOEL)	Skin irritation very slight in males at 24 mg, slight to moderate in M/ F at 240 mg and severe in M/ F at HDT. At all dose levels in males significant growth retardation, and decreased food intake and food efficiency. At HDT in males and females abnormal behavior and histopathological changes in the skin.
Mice M/F ⁶⁰	95	0, 50, 250, 1250 ppm ^a technical in diet	240 (NOAEL)	At HDT in males, a 25% increase in water consumption at week13, a 25% increase in BUN (vs controls) at 26 weeks, and a 17% increase in liver weight at week 26 only. At HDT in females a 10-16% increase in kidney weight, and an increase in urinary protein at week 52. Histopathology findings did not support a true toxic effect on the kidney in males or females..
Mice M/F ⁶⁰	28	0, 30, 60, 120, 240, 480 technical in diet	60 (NOEL)	In males at 120 mg liver changes of centri-lobular swelling and degeneration of hepatocytes; at 240 mg mild increases in liver enzymes, and at 480 mg single cell necrosis of the liver, significant increases in liver enzymes alkaline phosphatase, AST/SGOT, and ALT/SGPT, with liver enlargement and dark color.
Rabbit NSW M/F one each ²⁵	21	500 (2.1 mL) BEE dermal	only 1 dose tested	Severe effects limited to skin: moderate erythema, slight edema, distinct scaliness, slight to distinct necrosis, histopathology changes at necropsy.
Rabbit NSW F two per dose ²⁵	21	125, 250 (0.5, 1.0 ml) BEE dermal	125 (LOAEL)	Skin effects moderate at low dose and moderate to severe effects at HDT. Histopathology showed slight to moderate lesions of the skin.

Table 4-4 (cont.): Sub-chronic Toxicity of Triclopyr to Mammals

Test animal	Study Duration (days)	Doses Tested (mg/kg-day)	Dose (endpoint) (mg/kg-day)	Observed effects
Rabbit NSW 5 M 5 F ³³	7	1200 (M), 2000, 5050 technical to intact skin	2,000 (NOEL)	Erythema in 4/10. No mortality, signs of clinical toxicity, or weight gain. Abnormal lung and kidney necropsy findings in 5/10. No significant effects on body weight, food consumption, hematology, clinical chemistry; decreased PSP excretion at HDT.
Dog beagle M/F 4 each dose, sex group ⁶¹	365	0, 0.5, 2.5, 5.0 technical (98.9% a.i.)	0.5 (NOAEL)	In males and females no significant effects on mortality, clinical signs, body weight, or food consumption at any dose. Statistically significant increase in creatinine in 30% of males and 55% of females at 2.5 mg, and in 40% of males and 44% of females at 5.0 mg at 12 months. Significant increases in BUN at 2.5 even greater at 5 mg. Decrease in PSP excretion at 2.5 and 5.0 mg. No histopathologic changes in the kidney.
Dog beagle M/F 4 each dose, sex group ⁶²	184 F 183 M	0, 0.1, 1, 0.5, 2.5 technical in diet	> 2.5 (NOEL and LOEL)	No significant effects on body weight, food consumption, hematology, or clinical chemistry in male or females. At 2.5 mg decreased PSP excretion.
Dogs beagle M/F M/F 4 each dose, sex group ⁶³	228	0, 5, 10, 20 technical In diet	< 5 (NOEL) 5 (LOEL)	In females, decreased body weight and food consumption at all levels and slight thinning of coat hair at 10 and 20 mg. Decrease in hemoglobin, hematocrit, and red blood cell count in males and females at 20 mg/kg/day. Increased ALT/SGPT in all females at all levels and in males at 20 mg; increased AST/SGOT in males and females at 20 mg. Decreased PSP excretion in males and females at all dose levels. ^b At necropsy decreased amounts of adipose tissue in females at 20 mg/kg/day; histopathology of minimal (reversible) degenerative changes in liver and kidneys in males and females at all dose levels.
Dogs beagle M/F M/F 4 each dose, sex group ⁶⁴		0.5, 2 in gelatin capsule	0.5 M (NOAEL)	A supplemental study reported with the previous study. 2 mg resulted in a slight inhibition of PSP which was reversible after a minimum of 10 days.
Monkey Rhesus 8 M ²⁸	28 102	5 20 by gavage	<5 (NOAEL)	Body weight increase; no changes in BUN ; initial slight increase over baseline in creatinine but no impact with repeated doses. Slight non-significant decrease in PSP excretion after 8 days at 5 mg; at day 24 exceeded baseline and in no case was it significantly reduced.

Table 4-4 (cont.): Sub-chronic Toxicity of Triclopyr to Mammals

Test animal	Study Duration (days)	Doses Tested (mg/kg-day)	Dose (endpoint) (mg/kg-day)	Observed effects
Shetland pony 6 each dose, 3 controls ⁶⁵	4	0, 60, 300 by gavage	60 (NOEL)	At HDT depression, recumbency, decreased GI activity, labored respiration, ataxia, stiffness, fine tremors. Pale liver with hepatosis, fatty changes. Kidney swelling, casts in renal tubules, increased BUN. ^b Two of six died and two of six euthanized on days 5 and 6.
Holstein Cow ²⁷	4	5 ppm of 22.7 kg/day in feed (113.5 mg/day, for a total dose of 454 mg)	Not stated	Milk, urine, feces collected daily up to 6 days post dosing. 86.4% excreted unchanged in the urine with daily amounts in the first five days of 80.8, 94.9, 110.2, 102.8 and 4.0 mg. No residues found in milk or feces. No adverse effects reported.

HDT = Highest dose tested; M = male; F = female; BUN = blood urea nitrogen: along with creatinine, measures the kidney's ability to filter out waste products of protein metabolism.; PSP = phenolsulfophthalein.; AST = aspartate aminotransferase, also known as SGOT (serum glutamic oxaloacetic transaminase) and ALT = alanine aminotransferase also known as SGPT (serum glutamic pyruvic transaminase) are enzymes normally inside liver cells that enter the blood stream when the liver is damaged.

^a Equivalent to 5.55, 28.6, 143 mg/kg in males and 5.09, 26.5, 135 mg/kg in females.

^b A 38-day supplemental study suggested the existence of a competitive mechanism of renal excretion for the triclopyr and PSP dye at dose levels of 1 or 2, but not 0.5, mg/kg/day.

The EPA classified triclopyr as Group D (not classifiable as to human carcinogenicity) in 1998 based on a consensus recommendation of the agency's Carcinogenicity Peer Review Committee (CPRC). The CPRC's review found the animal evidence to be marginal (not entirely negative, but yet not convincing) and not supported by additional data from structural analogs or genotoxicity data.⁹ This decision was strongly criticized by The Northwest Coalition for Alternatives to Pesticides (NCAP)⁶⁶ citing the 1986 EPA guidelines requiring a compound to be classified as a carcinogen if it caused cancer in two species of laboratory animals.⁶⁷ The latest revised guidelines are more lenient, allowing the EPA to exercise considerable judgment in developing the ranking based on the nature and quality of the data.⁶⁸

For non-cancer chronic effects, the EPA established the RfD based on a NOEL of 5 mg/kg-day for parental/ systemic toxicity in a two-generation study in rats based on the observation of proximal tubular degeneration of the kidneys of P1 and P2 parental rats at the next highest dose of 25 mg/kg/day (see Table 4-5).

Table 4-5: Chronic Toxicity of Triclopyr to Mammals

Test animal	Study Duration	Doses Tested (mg/kg-day)	Dose endpoint (mg/kg-day)	Observed effects
Mice ICR M/F ⁶⁰	95 weeks	0, 50, 250, 1,250 ppm ^a technical (98.0% a.i.) in diet Equivalent to 0, 5.55, 28.6, 143 mg/kg-day (M) and 0, 5.09, 26.5, 135 mg/kg-day (F)	28.6, M (NOEL) 26.5, F (NOEL)	In males at HDT (143 mg), 25% increase in water consumption by week 13; 25% increase in BUN at 26 weeks; 17% increase in liver at week 26 only. In females at HDT (135 mg) 10-16% increase in liver weight, and in urinary protein at week 52. In females a significant increasing trend in mammary gland adenocarcinomas (p<0.05). No compound-related tumors in males. mice. Authors state no changes in kidney histopathology that support a true toxic effect on the kidney. NOEL based on decreased body weight gain.
Rat Fischer 344 M/F ⁶² 50 each sex per dose group ⁶⁹	2 years ^b	0, 3, 12, 36 Technical (98.0% a.i.) in diet in diet	12, M (NOEL) 36 F (NOEL)	In males at 3 and 12 mg a significant increase in adrenal medulla benign pheochromocytoma and benign/malignant pheochromocytoma combined, and in skin papillomas and subcutaneous fibromas. In females signif.cant trends in mammary gland adenocarcinoma and adenomas/ adnenocarcinoma combined. In males at the HDT a significant 10-17% increase in kidney weight with a dose-related trend at 12 months. In males at 12 and 26 mg increased proximal tubule degeneration at 6 months. Increased pigmentation of proximal descending tubule (kidney) in females at all dose levels. Significant decrease in hemoglobin and hematocrit at 6 months and in red cell count and hematocrit at 12 months.

HDT = highest dose tested; M = male; F = female; BUN = blood urea nitrogen.

^a Equivalent to 5.55, 28.6, 143 mg/kg/day in males and 5.09, 26.5, 135mg/kg/day in females.

^b Additional groups of 10 rats/sex/dose group exposed to same dose levels sacrificed at 6 and 12 months.

4.3.1.E Reproductive and Developmental Toxicity of Triclopyr

There are no reproductive studies of triclopyr in the open literature and only one of TCP, the major metabolite of triclopyr.⁷² The discussion below relies on unpublished reports described in the USDA Forest Service review⁵ and EPA RED.⁹

There are much more data on reproductive effects of triclopyr compared to other effects. Several studies found adverse maternal and development outcomes, including fetal malformations (see Table 4-6). Maternal toxicity was high, and the most severe adverse outcomes were found at the highest dose tested (HDT) of 100–300 mg/kg-day. A study of the reproductive and developmental effects of TCP, the major metabolite of triclopyr, found no adverse effects on fetal developmental or malformations in either rats or rabbits, even at dose levels that produced maternal toxicity.

Most of the studies of reproductive and developmental effects of triclopyr in the rat and rabbit find changes associated with maternal toxicity—decreased body weight and feed consumption in both species. More severe effects were found in rats, including rough hair, excessive shedding, salivation, difficulty breathing, tremors and abdominal discomfort at higher doses and death at the highest doses. Decreases in fetal weight and skeletal and ossification changes were found at dose levels associated with mild to moderate maternal morbidity. Major malformations occurred at levels that also cause severe maternal toxicity.

Other maternal effects reported were increased relative kidney weight in the rat and rabbit, and degeneration of the proximal tubules in the rat were found, and well as increased liver weight in both species. Lowered fertility, decreased uterine weight, and decreased numbers of litters and implantations were found in some studies.

Adverse effects on fetal and neonatal growth and development were also associated with maternal toxicity and were dose related. In rats at the highest doses tested decreases in pup weight, survival, litter size, and resorptions (abortion), minor skeletal and ossification changes were found; there were no changes in sex ratio. Major malformations were only found in litters with severe maternal toxicity. In three of four studies in the rabbit no major malformations were found even at maternally toxic levels. At dose levels 100 mg/kg an increase in resorptions (abortion), fetal deaths, and skeletal and ossification anomalies were found. A non-statistically significant increase in central nervous system anomalies at the highest doses tested in one study was also found in controls. The studies are summarized in Table 4-6 below.

Table 4-6: Reproductive and Developmental Toxicity of Triclopyr to Mammals

Test animal	Study Duration	Doses Tested (mg/kg-day)	Dose (endpoint) (mg/kg-day)	Observed effects
Rats S-D M/F 30 each sex and dose ⁷⁰	2 gen P ₁ 10 weeks P ₂ 12 weeks	0, 5, 25, 250 technical (99.4% a.i.) in diet	5 (NOEL) parental 25 (NOEL) fertility, neonatal (pups)	No adverse effects adult or neonatal M/F at 5 mg. At 25 mg increase relative kidney weight in P ₁ M and at HDT in P ₁ and P ₂ M/F. At 25 mg in both P ₁ /P ₂ adults, degeneration of renal proximal tubules in some M/F at 25 mg and in the majority at HDT. No changes in reproductive organ M/F adults at any dose. At HDT in adult M/F decreased feed consumption and body weight, increased liver weight but no histopathology changes. At HDT significant decrease in pup weight, survival, and litter size in both F ₁ ,F ₂ . Lower fertility and conception rates in F ₁ ,F ₂ generation attributed to females since no effect found on spermatogenesis. Increased incidence of F ₂ pups with exencephaly and ablepharia at 25 mg.
Rats S-D M 11-12 per dose F 23 per dose ^{71,72}	3 gen	3, 10, 30 Technical in diet	< 3 (NOEL) maternal and developmental	No effect on reproductive capacity, growth, or maturation. At 3 mg, third generation pups in one litter appeared weak and evidenced retarded growth, associated with non-functioning mammary glands in the dam. No similar effects at higher doses.
Rats S-D time mated ⁷³	Days 6-15 of gestation	0, 30,100, 300 TEA (46.5%) by gavage	30 (NOEL) maternal 100 (NOEL) developmental	At HDT clinical signs of maternal toxicity and one death. Developmental toxicity at HDT of decreased body weight, increased skeletal anomalies (reduced ossification, unossified sternebrae).
Rats S-D M/F 25 per sex per dose ^{74,75}	Days 6-15 of gestation	0, 50, 100, 200 Technical by gavage	< 50 (LOAEL) maternal 100 (NOAEL) developmental	At all dose levels maternal toxicity—signs of rough hair, salivation, occasional dyspnea and tremors, and abdominal discomfort. At 100 and 200 mg food consumption and weight gain significantly depressed. No significant effects on implantations, viable fetuses, resorptions, or corpora lutea, fetal body weights or sex ratios. Litters of 200 mg dams had significant increase in retarded ossification of the skull bones, and 2 had major malformations (considered equivocal). Doses of 50 or 100 mg mildly toxic to dams but did not appear to cause adverse effects in developing fetuses.

Table 4-6 (cont.): Reproductive and Developmental Toxicity of Triclopyr to Mammals

Test animal	Study Duration	Doses Tested (mg/kg-day)	Dose (endpoint) (mg/kg-day)	Observed effects
Rats S-D F adults ⁷⁶	Days 6-15 of gestation	0, 50, 100, 200 tech. (98.5%) by gavage	100 (NOEL) maternal and developmental 200 (LOEL) maternal and developmental	Dose-related, transient maternal toxicity (roughening of hair, excessive shedding) in all dose groups. At 100 and 200 mg body weight decreased 13% and 17% and food consumption. No significant effects on corpora lutea, implantations, or litter size. At 200 mg, increased resorption (complete resorption one entire litter only). A slight, non-significant decrease in fetal body weight HDT; two fetuses with cleft palate, brachycephaly (short broad head), and skeletal abnormalities. Minor soft tissue and skeletal variations observed in control and treated groups.
Rats CD, time-mated F ⁷⁷	Days 6-15 of gestation	0, 30, 100, 300 TEA by gavage	30 (NOEL) maternal	At 100 mg maternal morbidity with weight loss, increased water and decreased feed consumption. At HDT marked maternal morbidity, mortality, and increased kidney weights; fetal effects of decreased weight and delayed ossification. No teratogenic effects.
Rats CD time-mated F, 25 per dose Phase I; 30 per dose Phase II ^{78,69}	Days 6-15 of gestation	0, 30, 100, 300 BEE (97.0%) by gavage Phase I^a 0, 5, 30, 100, 300 BEE (97.0%) by gavage Phase II^a	100 (NOAEL) maternal and developmental 300 (LOAEL) maternal and developmental	Phase I:^a At HDT marked maternal toxicity with 4 four deaths, in a few dams, mean weight loss, decreased feed and increased water consumption, and increased mean liver and kidney weights, and increase in late <i>in utero</i> deaths. At all doses, slight reduction in weight gain and clinical signs of toxicity. At 100 mg, increased water consumption, decreased uterine weight and litter weight (not dose dependent). Dose-related increase in litters with malformed fetuses: 2 of 25 at 0 mg, 1 of 23 at 30 mg, 3 of 24 at 100 mg, 6 of 16 at 300 mg, with microphthalmia, anophthalmia, retinal folding, cleft palate, other craniofacial abnormalities (misshapen lower jaw, hydrocephaly, rhinencephaly, agnathia). Malformed litters were from dams with the most severe signs of toxicity at HDT. decreased fetal weight, increased fetal and litter incidence of skeletal anomalies, increased fetal incidence of unossified sternebrae. Phase II:^a The only litter effect seen in both Phase I and Phase II was an increase in extra ribs at HDT; severe malformations were not seen.
Rabbit NZW F ⁷⁹	Days 6-18 of gestation	0, 25, 50, 100 tech. by gavage	< 25 (NOAEL) maternal 100 (NOAEL) developmental	At all dose levels, maternal toxicity and mortality observed, but no toxicity to the developing embryo and fetus. No major malformation or soft tissue anomalies found at any dose level.
Rabbits NZW sexually mature F ⁷⁶	Days 6-18 of gestation	0, 10, 25 tech (98.5%) by gavage	Not stated	Transient, dose-related decreases in maternal body weight gain. No signs of treatment-related effects on fetal growth or development.

Table 4-6 (cont.): Reproductive and Developmental Toxicity of Triclopyr to Mammals

Test animal	Study Duration	Doses Tested (mg/kg-day)	Dose (endpoint) (mg/kg-day)	Observed effects
Rabbit NSW F ⁸⁰	Days 6-18 of gestation	0, 10, 30, 100 TEA by gavage	10 (NOEL) maternal 100 (NOEL) developmental	At 100 mg severe maternal toxicity and mortality, including weight loss, decreased feed consumption, and increased liver and kidney weights. Increased abortions attributed to maternal toxicity. At 30 mg increase in abortions and early deliveries were associated with weight loss or anorexia in affected dams. No developmental or teratogenic effects at any dose level.
Rabbit NSW F ⁸¹	Days 6-18 of gestation	0, 10, 30, 100 BEE by gavage	30 (NOEL) maternal and developmental	At 100 mg, severe maternal morbidity including weight loss and decreased feed consumption, and mortality; increased resorption, decreased litter size and litter weight, and increases in minor skeletal alterations (additional sterbral centers, reduced ossification of digital bones, and extra ribs). No teratogenic effects even at maternally toxic dose
Rabbit NZW F ^{81, 69}	Days 6-18 of gestation	0, 10, 30, 100 BEE tech. (96.9%) by gavage	30 (NOEL) maternal 100 (LEL) maternal	At HDT, maternal and developmental toxicity with decrease in number of live fetuses, decrease in number of live fetuses per dam, significant increase in post-implantation loss, increase in fetal deaths an increased number of fetal and/or litter incidence of skeletal anomalies and variants (reduced ossification of sacrocaudal vertebral arches and cranial centers, and unossified sternbrae).
Rabbits NZW F ⁸²	Days 6-18 of gestation	0, 10, 30, 100 TEA (46.5% a.i.) by gavage	30 (NOEL) Maternal and developmental 100 (LOEL) maternal	Maternal toxicity at 100 mg/kg with increased mortality during test administration, decreased weight gain and food efficiency, and increased liver and kidney weights. Developmental toxicity at 100 mg/kg with decreased numbers of litters, corpus lutea, total implants, total live fetuses and increased embryonic deaths, deaths per dam, and increased pre-implantation loss.
Rabbit NZW 16 F inseminated ³¹	Days 7-19 of gestation	0, 25, 100, 250 TCP ^b by gavage	25 (NOAEL)	AT HDT maternal mean weight loss of 70 grams (140 in controls); no clinical signs of toxicity. Fetuses evaluated on gestation day 28. No effect on fetal weight or viability. A non-statistically significant increase in central nervous system anomalies (also found in controls).

Table 4-6 (cont.): Reproductive and Developmental Toxicity of Triclopyr to Mammals

Test animal	Study Duration	Doses Tested (mg/kg-day)	Dose (endpoint) (mg/kg-day)	Observed effects
	Acute RfD for general population		100 mg/kg-day/ (10*10) ^c = 1.0 mg/kg-day	RfD based on developmental toxicity test in rats, where unspecified “clinical signs” were observed on GD 7 at the next highest dose of 300 mg/kg-day. Study done with triclopyr BEE.
	Acute RfD for women age 13–50 (childbearing age)		5 mg/kg-day/ (10*10) ^c = 0.05 mg/kg-day	RfD based on increased incidence of F2 rat pups with exencephaly (brain located outside of skull) and ablepharia (absence of eyelids) at the LOAEL of 25 mg/kg-day. Study done with triclopyr acid.
		Chronic RfD	5 mg/kg-day/ (10*10)^c = 0.05 mg/kg-day	RfD based on increased incidence of proximal tubular degeneration in the kidney in male and female P1 and P2 rats at the next highest dose of 25 mg/kg-day. Study done with triclopyr acid.

S-D = Sprague Dawley; NZW = New Zealand White; GD = gestation day; M = male; F = female; RfD = Reference dose.

Shaded rows are the studies on which the RfD is based. **Bolded rows summarize the acute and chronic RfDs.**

^a Separate studies. Phase II conducted to assess the reproducibility of effects seen in Phase I.

^b 3,5,6-Trichloro-2-pyridinol, the primary metabolite of triclopyr.

^c Intraspecies uncertainty factor of 10 and interspecies uncertainty factor of 10.

4.3.1.F Neurotoxicity

There are no studies designed to detect potential adverse effects on the central or peripheral nervous system in mammals exposed to triclopyr. The neurological effects observed in rats, mice, rabbits, and dogs—lethargy, impaired coordination, weakness, labored respiration, and tremors—discussed above, were only observed at very high toxic doses, and may be secondary to effects on other affected body systems.

4.3.1.G Immunotoxicity

The powerful protective immune system is highly complex and interacts with all other body systems. The only way to determine potential immunotoxic effects of triclopyr is to directly study its effects on the immune system, including lymphoid tissue (lymphoid nodes, thymus), bone marrow, lymphocytes (B-cells and T-cells), antibodies, immunoglobulins, among and other components.

No reports of any abnormalities in lymphoid tissues were found in the studies reviewed for this summary, except thymic enlargement in mice in one study.⁶² The only studies related to the immune system that have been performed with triclopyr are those testing skin sensitization (delayed hypersensitivity, allergy) in rabbits and guinea pigs—one found sensitization but most did not (see Table 4-3).

The Forest Service review notes:

“In these reviews of the toxicity of triclopyr, morphologic abnormalities in lymphoid tissues – indicative of potential damage to the immune system – have

not been reported. Since histopathologic evaluations of lymphoid tissues and evaluation of blood leukocyte counts are standard procedures in most rodent bioassays and since positive effects in these tissues would typically be reported prominently, it is reasonable to assert that these effects were not noted in the many standard bioassays of triclopyr.”

“Equally important is the fact that the most sensitive effect for triclopyr is well characterized and involves damage of proximal tubular tissue of the kidneys. This is the endpoint selected by U.S. EPA as the basis for the RfD and is the same endpoint used in the SERA risk assessment for triclopyr. Protecting against this critical effect using the existing RfD is considered to be protective of all toxic effects and there is no specific information on the potential immunologic effects of triclopyr that raises significant questions concerning the protectiveness and adequacy of the current RfD” (page 27).⁸³

4.3.1.H Endocrine Disruption

The studies on reproduction and development in rats and rabbits suggest that triclopyr is not an endocrine disruptor, but it has not been studied for its potential to interact or interfere with estrogen, androgen, thyroid or other endocrine organ hormone systems. A European Union survey of the scientific literature on endocrine effects of pesticides does not list triclopyr as a chemical of concern,⁸⁴ nor do other sources of information on endocrine disrupting effects.⁸⁵ The surfactants Competitor and Sylgard 309 that are being considered for use in this project do not contain the known endocrine disruptors nonylphenol or nonylphenol ethoxylate. However, no comprehensive evaluation of triclopyr or these surfactants has been undertaken, and no final conclusions on the endocrine disrupting ability of these compounds can be drawn at this time. Triclopyr is not one of the first set of chemicals slated for testing of endocrine disrupting effects by the EPA. It is not clear when testing on this herbicide will be done.

4.3.1.I Effects on Mammalian Wildlife

US EPA's Ecotox database does not contain any field studies on the effects of triclopyr on wild mammals. One study found that white-tailed deer avoided areas treated with herbicides followed by burning, but this avoidance may have been due to other factors besides herbicide treatment.⁸⁶ At normal field application rates of triclopyr, no adverse effects have been noted on reproductive activity in mammals, although few studies have been done.⁸⁷

4.3.1.J Levels of Concern for Mammals

The acute TRV for triclopyr in mammals is based on a NOAEL in a developmental toxicity study in rats of 100 mg/kg-day, where unspecified “clinical signs” were observed on GD 7 at the next highest dose of 300 mg/kg-day. The chronic TRV for mammals is based on a NOAEL of 5 mg/kg-day for parental/ systemic toxicity in a two-generation study in rats based on the observation of proximal tubular degeneration of the kidneys of P1 and P2 parental rats at the next highest dose of 25 mg/kg/day. No adjustments of these values were performed to make them more protective.

The USFS notes that:

“The application of these NOAEL and LOAEL values to small rodents is clearly appropriate, since the NOAEL and LOAEL values come from studies in rats. Ecological risk assessments, however, are intended to encompass a wide range of mammalian species, from very small animals such as mice and voles to large mammals such as deer. For many chemicals, systematic differences in species sensitivity are apparent and generally indicate that small animals are less sensitive (i.e., have higher toxicity values) than large animals. For triclopyr, the best study in a large mammal for quantitatively comparing differences in sensitivity is the study by Osweiler (1983 summarized in Appendix 4) in which adult Shetland pony geldings weighing 151-203 kg were given gavage doses of triclopyr at 0, 60, and 300 mg/kg/day for 4 days. As in the rodent studies, the dose of 300 mg/kg/day was clearly a LOAEL – i.e., horses evidenced gross toxicity including depression and recumbency as well as kidney damage. At 60 mg/kg, no adverse effects were noted. Thus, this study suggests that larger mammals are no more sensitive to triclopyr than smaller mammals, although dogs may be an exception (Section 3.3.2).”

4.3.2 Other Terrestrial Organisms

Triclopyr ranges from not acutely toxic to slightly acutely toxic to birds and honeybees. There is no information on non-honeybee insects. Trace amounts of triclopyr (<0.5% of application rate) can be toxic to non-target plants and possibly toxic to bryophytes (mosses). The maximum permissible application rate of Garlon 4 Ultra to brush and forests is 9 kg/ha, and 4.5 kg/ha for perennial weeds. There is some evidence that triclopyr is mildly toxic to mycorrhizal fungi at these application rates.

The TRVs for terrestrial organisms are summarized in Table 4-8. Toxicity studies reported in this section are summarized in Table 4-9. An extended presentation of the data in Table 4-9 can be found in Appendix E.

4.3.2.A Birds

On an acute basis, triclopyr has been classified as slightly toxic to birds. The EPA chemical registration studies provide most of the available data on avian toxicity, including reproductive toxicity. Triclopyr appears to be moderately toxic to avian reproduction.

The eight-day oral LD₅₀ values for triclopyr ranges from 510 to 1,700 mg/kg of organism body weight. The LC₅₀ values range from 2,930 to 6,700 mg a.e./kg of food.¹¹ Studies used Garlon 4 (formulation of triclopyr butoxyethyl ester and a kerosene solvent), triclopyr butoxyethyl ester and triclopyr triethylamine salt. Although there are only a few studies to compare, there does not appear to be a large difference in the toxicity of triclopyr TEA and triclopyr BEE in birds. US EPA determined LC₅₀ values of 5,360 and 3,880 mg a.e./kg food for mallards for the TEA and the BEE compounds, respectively, equivalent to LD₅₀ values of 536 and 388 mg/kg-day. The lowest LC₅₀ value reported by EPA for triclopyr acid (formed when both triclopyr TEA and BEE dissolve or degrade in the environment) is 1,480 mg/kg food, which would result in an LC₅₀ of 148 mg/kg body weight. There is also a lower LC₅₀ for triclopyr TEA of 4,660 mg/kg food (466 mg/kg body weight). For a summary of all available studies, see Table 4-9 and Appendix E, Table E-2.

Avian reproductive studies were conducted for triclopyr as part of the EPA registration process. The LOEC for weight loss and decreased reproductive success in birds is 500 mg/kg of food.⁸⁸ Based on the USFS assumption that birds eat about 10% of their body weight per day, 500 mg/kg food corresponds to a dose of approximately 50 mg/kg body weight. At this dose, statistically significantly fewer offspring survive to be 14 days old. The avian reproductive NOAEL for triclopyr is 10 mg/kg of body weight. A summary of these results can be found in Table 4-9 and Appendix E, Table E-3.

Levels of concern for birds: The USFS uses the EPA's LC₅₀ values for mallards exposed to triclopyr BEE of 3,880 mg a.e./kg food as the basis of the acute TRV. An adjustment of 10% is applied to estimate the amount of food a bird eats. The resulting LD₅₀ value is 388 mg a.e./kg body weight, which is used as the acute TRV. This is not an especially protective TRV because doses at this level could result in mortality of 50% of birds exposed, which is unacceptable. Furthermore, this LC₅₀ value is not the lowest LC₅₀ reported by EPA (see above). We therefore divide the TRV by a factor of six, according to EPA's methodology for protecting endangered species²¹ to obtain 65 mg/kg as the acute TRV used in the MMWD risk assessment.

The chronic avian TRVs are derived from the EPA reproductive NOAEC values of 100 mg a.e./kg food for triclopyr acid in mallard ducks. To convert this from concentration in food to a dose in mg/kg body weight, a conversion factor of 10% is applied. The final chronic TRV used for the MMWD assessment for triclopyr BEE is 10 mg a.e./kg.

The same acute and chronic TRVs are used for triclopyr TEA.

4.3.2.B Terrestrial Invertebrates

EPA classified triclopyr as not acutely toxic to honeybees, the only terrestrial invertebrate for which there is information in the Ecotox database. Acute contact toxicity studies in honeybees give LD₅₀ values that range from 25 to over 100 µg/bee. See Table 4-9 and Appendix E, Table E-4 for a summary of honeybee studies.

Levels of concern for bees: The USFS used a 100 µg/bee LD₅₀ for triclopyr acid as the TRV for honeybees. A bee was assumed to weigh 0.000093 kg, corresponding to a TRV of 1,075 mg/kg body weight. This value was deemed insufficiently protective because it did not correct for the fact that the TRV is derived from an LD₅₀ and not a NOEL. For the MMWD analysis, the LD₅₀ was divided by six to give a TRV of 179 mg/kg for the MMWD assessment. The same TRV is used for triclopyr TEA.

4.3.2.C Terrestrial Plants

As a selective herbicide for controlling broadleaf plants, triclopyr is toxic to many non-target plant species. Triclopyr and other pyridinecarboxylic acid herbicides (*e.g.* picloram and 2,4-D) mimic indole auxin plant growth hormones. Auxins help control plant growth; triclopyr disrupts the system by causing uncontrolled growth. At sufficiently high levels of exposure, the abnormal growth is so severe that vital functions cannot be maintained and the plant dies.^{89a, b, c, d} Triclopyr BEE is more toxic to plants than triclopyr acid for seedling emergence and approximately the same toxicity in vegetative vigor studies.

For all herbicides, US EPA requires manufacturers to perform seedling germination and emergence and vegetative vigor studies in non-target plants (including effects on corn and soybean). The EPA reregistration decision summarizes these studies for both triclopyr TEA and triclopyr BEE.⁹ Seedling germination studies involve submersion of seeds in solution with triclopyr. Both of these tests simulate the effects of herbicide-contaminated runoff on emergent vegetation. Vegetative vigor studies involve direct foliar applications to young plants and simulate the effects of spray drift.

Triclopyr BEE has similar toxicity in both the seedling emergence and vegetative vigor assays, with the lowest NOEC being 0.0022 lbs a.e./acre for seedling emergence in onions and 0.0029 lbs a.e./acre for vegetative vigor in sunflowers. The requirement for a seedling germination test was waived for triclopyr BEE. Triclopyr TEA is much less toxic than triclopyr BEE in the seedling emergence assays (seeds were in solution), with an NOEC of 0.23 ppm in corn and radishes. However, triclopyr TEA is nearly the same as the BEE compound in the vegetative vigor assay in sunflowers, with a NOEL of 0.0030 lbs a.e./acre. The lowest EC₂₅ and NOEL values for seedling germination were for sugar beets: 0.00052 and 0.00015 ppm a.e., respectively. Seedling germination EC₂₅ values and NOELs were 20-50 times higher for corn. Since corn is a monocot and triclopyr works more effectively on dicots, corn is relatively insensitive to triclopyr exposure.

The higher toxicity of triclopyr BEE in the seedling emergence assay may be due to the more rapid absorption of BEE relative to TEA. This difference has been demonstrated quantitatively for chickweed, wheat, and barley,⁹⁰ and is likely to hold true for other plant species. As discussed in USFS 2003, variations in species sensitivity to triclopyr BEE appear to be related directly to the rate of metabolic ester hydrolysis by the plant.⁹⁰

Water availability to the plant may also affect triclopyr's herbicidal efficacy. Although arid conditions do not affect the rate of triclopyr absorption, efficacy is reduced due to an inhibition of translocation of the herbicide in the plant.^{91a,b} This is relevant to the MMWD vegetation management project, since if herbicides are used, they would only be used in the dry season between May 15 and September 15.

One study suggests that some bryophytes and lichens may suffer long-term effects after triclopyr exposure.⁹² The EC₅₀ for a decrease in relative abundance six months after application is about 1 kg/ha. The statistical analyses presented in reference 92 involve the use of a non-threshold polynomial model. Since the effect being measured does involve a threshold—death of the plant—this may not be the most appropriate statistical model for the study. Nonetheless, reference 92 appears to present a plausible basis for concern that exposure to substantial triclopyr drift may have long-term impacts on bryophyte and lichen communities.

Levels of concern for terrestrial plants: There is an abundance of information on the toxicity of triclopyr to plants, showing that triclopyr is far more toxic to dicots than monocots or conifers. For assessing the potential consequences of exposures to non-target plants via runoff, USFS used the NOEC values for seedling emergence for triclopyr BEE (0.003 lb a.e./acre) and triclopyr TEA (0.333 lb/acre). For assessing the impact of drift, USFS used bioassays on vegetative vigor,

with NOEC values of 0.0039 lb/acre for triclopyr BEE and 0.0041 lb/acre for triclopyr TEA. We used the same TRVs for the MMWD assessment.

4.3.2.D Soil Microbes

There is little information on the toxicity of triclopyr to terrestrial microorganisms. Garlon 4, at concentrations of 0.74 ppm in growth medium (agar) over 26–48 days, can inhibit growth in the mycorrhizal fungi *Pisolithus tinctorius*, and *Hebeloma longicaudum*.⁹³ Mycorrhizal fungi are symbionts with plants that provide water and mineral nutrients in exchange for plant carbohydrates. *Cenococcum geophilum*, the slowest growing fungus, was least sensitive to the effects of triclopyr, exhibiting decreased growth at 742 ppm a.e. A similar study found that triclopyr (formulation not reported) could inhibit growth in five mycorrhizal species: *Hebeloma crustuliniforme*, *Laccaria laccata*, *Thelophora americana*, *Thelophora terrestris*, and *Suillus tomentosus*.⁹⁴ Fungi were kept in liquid culture for 30 days and the reduction of biomass with increasing triclopyr concentrations was measured. A 90% reduction in biomass was observed for all species at concentrations of 720 ppm; greater than 50% reduction biomass was observed in four of the five species at 36 ppm. The most sensitive species, *Thelophora americana*, exhibited a 6% decrease in growth rates relative to controls at triclopyr concentrations of 0.072 ppm (this result was statistically significant). In other species, statistically significant decreases in growth were reported between 0.72 ppm and 7.2 ppm.⁹⁴ Soil concentrations of triclopyr are typically 4–18 ppm following application of 0.28–10 kg/ha.⁹³ At realistic application rates, triclopyr could affect some fungal communities, but the data are sparse, and there is significant uncertainty about the potential effects of triclopyr on soil microorganisms.

The USFS used GLEAMS modeling to estimate long-term concentrations of triclopyr in soil over time, estimating that an application rate of 1 lb/acre would result in long-term soil concentrations that are well below 0.1 ppm—in the range of 0.02 to 0.05 ppm. Peak concentrations would be in the range of about 0.2 ppm. The USFS concludes that transient inhibition in the growth of some bacteria or fungi might be expected, which could result in a shift in the population structure of microbial soil communities but substantial impacts on soil would not be anticipated.

Levels of concern for soil microbes: There are no soil microbe exposure models available. Further, endpoints varied considerably in the available toxicity data. Some species showed inhibited growth at 740 ppm a.e., and similar effects were observed on other species with doses as low as 0.074 ppm a.e. The USFS did not develop a TRV for soil microbes, indicating that there is insufficient information to model triclopyr hazards to soil microbes.

4.3.3 Aquatic Organisms

Triclopyr aquatic toxicity varies by product formulation. The triethylamine salt of triclopyr, the active ingredient in Garlon 3A, is classified as not acutely to slightly toxic to fish, amphibians and aquatic invertebrates. The butoxyethyl ester is considered moderately to highly acutely toxic to fish, moderately acutely toxic to amphibians and moderately to highly acutely toxic to aquatic invertebrates and aquatic plants. There is less information on the toxicity of triclopyr to amphibians, in part because the EPA does not require amphibian studies for registration. Toxicity data for both triclopyr BEE (active ingredient in Garlon 4 Ultra) and triclopyr TEA (Garlon 3) are presented here. Triclopyr BEE TRVs are used for determining levels of concern

for acute scenarios such as spills and peak runoff, since this is the active ingredient under consideration for use in the MMWD watershed. For long-term runoff where several months might pass before a rainstorm with sufficient volume to cause runoff occurs, TRVs for the degradation product 3,5,6-trichloro-2-pyridinol (TCP) are used. Aerobic degradation of triclopyr in soil produces the metabolites TCP, 3,5,6-trichloro-2-methoxypyridine (TMP) and CO₂.⁹⁵ In a lab soil-column study, the relative amounts of these products at 54 days were 4% triclopyr, 88% TCP, and 15% TMP for triclopyr acid-treated soil. For triclopyr BEE-treated soils, concentrations were 6% triclopyr, 88% TCP and 7% TMP.⁹⁶

4.3.3.A Fish

Triclopyr toxicity to fish varies by product formulation. Garlon 3, with active ingredient triclopyr TEA, is considered not acutely toxic to fish. In contrast, Garlon 4, with active ingredient triclopyr BEE, is moderately to highly acutely toxic. The toxicity of triclopyr acid is between that of the salt and the ester, due to its acidity and ability to lower the pH of a water body at high enough concentrations. The degradation product TCP is moderately acutely toxic. The available toxicity studies are summarized in Table 4-9 and Appendix E, Tables E-5 and E-6.

Triclopyr is one of the chemicals under review by EPA for its potential effects on endangered salmon, and as part of the review, EPA developed an endangered species risk assessment for federally listed Pacific salmon and steelhead.²¹ Expected environmental concentrations of triclopyr were modeled and compared to TRVs for fish, aquatic invertebrates and aquatic plants for different triclopyr use scenarios. EPA notes in the report:

The models indicated an exceedance of the direct acute risks to endangered and threatened fish for all registered uses of triclopyr BEE. Acute risks to invertebrates and aquatic plants was indicated for all uses that involve a direct application to six inches of water such as forest tree management and weed control to non-irrigation ditchbanks.

A review of the potential effects of triclopyr on salmon led EPA to conclude that triclopyr may adversely affect 16 of the 26 threatened and endangered salmon species in California and the Northwestern US.

Most of the available fish toxicity studies are from the chemical registration process and from Wan *et al.* 1989.⁹⁷ Table 4-7 summarizes the acute studies in Wan *et al.* 1989, providing a comparison between the Garlons, triclopyr TEA, triclopyr BEE and triclopyr breakdown products for acute toxicity. All toxicity endpoints are for rainbow trout, with the exception of the LOEC for triclopyr TEA, allowing for direct comparison between chemicals. Rainbow trout were chosen for comparison because the species is well-studied. All chronic toxicity studies are from the EPA AQUIRE database and reference 100. No studies are available for Garlon 4 Ultra specifically. Therefore, reports are presented for Garlon 4, which has the same active ingredient (triclopyr BEE) as Garlon 4 Ultra, but contains kerosene as a solvent/adjuvant. Results for Garlon 3 are also presented, since triclopyr TEA is similar in toxicity to triclopyr acid, which is formed on hydrolytic degradation of triclopyr BEE.

Table 4-7: A Comparison of the Relative Toxicity of Different Forms of Triclopyr, Garlon Formulations, and Degradation Products to Rainbow Trout

A.I./Product	96-hour LC ₅₀ (mg a.e./L)	Sub-lethal LOEC (mg a.e./L)
Triclopyr acid	7.5	NA
Triclopyr TEA	169-432	114-178 (fathead minnow)
Triclopyr BEE	0.81	NA
Garlon 3A (Triclopyr TEA)	420	141-564
Garlon 4 (Triclopyr BEE)	2.7	0.45-14.2
TMP	4.6	NA
TCP	1.5	NA

Data Source: Reference 97.

A comparison of 24-, 48-, 72-, and 96-hour LC₅₀ values for six salmonids shows that there is little time or species dependence in LC₅₀ values (see Table 4-9 and Table E-5 in Appendix E). However, there are remarkable differences in the toxicities of triclopyr TEA and triclopyr BEE, and these differences are magnified in the toxicities of the Garlon formulations. Triclopyr BEE has a 96-hour LC₅₀ value for rainbow trout of 0.82 mg a.e./L, an order of magnitude lower than that for triclopyr acid at 7.5 mg a.e./L. The results for the different Garlon products are even more striking. Garlon 4 has an LC₅₀ value of 2.7 mg a.e./L for rainbow trout, two orders of magnitude lower than that for Garlon 3A at 420 mg a.e./L. The toxicity of Garlon 4 is consistent with the toxicity of the active ingredient triclopyr BEE. The kerosene in Garlon 4 does not appear to contribute to the product's toxicity.⁹⁸

The 24-hour LC₅₀ values for Garlon 4 for six salmonids (coho, chum, chinook, pink and sockeye salmon and rainbow trout) in reference 97 are similar to other reported LC₅₀ values: 0.59–1.31 mg a.e./L⁹⁹ and 0.60 mg/L.¹⁰⁰ Data from reference 101 shows a strong time-dependent response among 1-hour, 6-hour and 24-hour LD₅₀ values, with most of the toxic effects of triclopyr BEE occurring in the first 24 hours of exposure. This effect is explained by the relatively rapid degradation of the higher toxicity triclopyr BEE compound compared to that of triclopyr acid produced on hydrolysis.

Sub-lethal effects of triclopyr on salmonid behavior and growth are observed at lower concentrations than acute effects, while confirming the relative acute toxicity rankings. Coho salmon were lethargic at concentrations of 0.24-0.32 mg a.e./L of Garlon 4 in 96-hour flow-through experiments.¹⁰⁰ The dose at which this sub-lethal effect occurred is approximately a factor of two below the 96-hour LC₅₀ determined in the same study. A LOEC of 0.074 mg a.e./L caused coho to be hypersensitive to stimuli over 4-day periods of exposure. Another study reports an almost identical LOEC for behavioral changes in rainbow trout: 0.44 mg a.e./L for Garlon 4, and also reports a much higher LOEC of 141 mg a.e./L for Garlon 3A.^{101,97}

Two studies evaluated long-term exposure of fathead minnows to triclopyr TEA.^{102a, b} The minnows were exposed to triclopyr from egg to fry (juvenile fish, less than a year old, with no egg sac and still in freshwater). Survival (embryo-larval stages) was significantly reduced at 178 mg a.e./L compared to control animals. At 114 mg a.e./L, there was a slight decrease in body length.

Environmental metabolites of triclopyr can be as toxic to fish as triclopyr acid or triclopyr BEE.¹⁰³ Breakdown products 2-methoxy-3,5,6-trichloropyridine (TMP) and 3,5,6-trichloro-2-pyridinol, (TCP), have LD₅₀ values that range from 1.1 to 6.9 mg/L and 1.8 to 2.7 mg/L, respectively, in salmonids (See Table 4-7 above. Note that Table 4-7 is almost exclusively for trout; see Table 4-9 and Appendix E for LD₅₀ values for all salmonids). The NOEC for TCP in juvenile rainbow trout is 0.081 mg/L, with a LOEC of 0.13 mg/L for reduced growth at early life stages.¹⁰³ Thus, TCP appears to be much more toxic than triclopyr TEA, which has corresponding LOEC values in juvenile fathead minnows of 114, 162 and 178 mg/L. It is unclear from the reference if these LOEC values are in units of active ingredient or acid equivalent.

Field studies show mixed results for triclopyr toxicity and persistence in the field. Mortality did not increase in caged fish in creeks in Ontario that received an aerial application of Garlon 4 at 4 kg/ha.¹⁰⁴ Nor did triclopyr bioaccumulate in edible fish tissue. However, another study found a bioconcentration factor (BCF) of one in bluegill sunfish.¹⁰⁵ In another study that used Garlon 3A in wetlands to control purple loosestrife, duckweed, *Daphnia*, and rainbow trout were unaffected.¹⁰⁶ In another study, all rainbow trout died by day three, when initially treated with 0.25-0.76 mg/L of triclopyr BEE in a large lake enclosure. This concentration was meant to simulate 3.84 kg/ha aerial spray over a lake 15-50 cm deep.

Levels of concern for fish: Triclopyr risk characterizations for aquatic life vary considerably between TEA and BEE formulations. The USFS assumed all triclopyr degrades to form the acid and based long-term runoff risk calculations on triclopyr. For the long-term runoff scenario in the MMWD watershed, we use TRVs for the primary degradate TCP, since it would be the dominant species under the application circumstances.

The acute TRV used by the USFS for triclopyr BEE is taken from the registration studies submitted to EPA—an LC₅₀ value of 0.25 mg a.e./L for bluegill. This is not an especially protective TRV because doses at this level could result in mortality of 50% of fish exposed, which is unacceptable. We therefore divide the TRV by a factor of 20, according to EPA's methodology for protecting endangered fish species²¹ to obtain a TRV for triclopyr BEE of 0.013 mg a.e./L for use in the MMWD assessment. We use a factor of 20 instead of a factor of six, because the results of several salmon studies that indicate that adverse effects to olfaction occur at pesticide concentrations 20 times lower than the LC₅₀.²³

There are very few studies on which to base a chronic fish TRV. The USFS uses the triclopyr acid NOEC of 104 mg/kg for the chronic TRV for both triclopyr BEE and TEA. The argument for using the same TRV for chronic exposure is that both forms of triclopyr degrade or dissociate to triclopyr acid. However, triclopyr TEA and acid degrade in the environment to form TCP with a half-life for degradation similar to that of triclopyr. The 96-hour LC₅₀ of the degradation product TCP is 1.5 mg/L. We use this value and divide by an adjustment factor of 20 for sensitive fish to obtain a chronic TRV of 0.075 mg/L for the MMWD assessment.

For triclopyr TEA, the USFS use an acute TRV of 199 mg/L based on an LC₅₀ for bluegill. Since a NOEC of 104 mg/L for fathead minnows was available for triclopyr TEA, we used this endpoint in the MMWD risk assessment as the acute endpoint for triclopyr TEA. The chronic

TRV is that for TCP of 0.075 mg/L, the same for both triclopyr BEE and triclopyr TEA because both chemicals degrade to TCP.

4.3.3.B Amphibians

As for fish, Garlon 3A (triclopyr TEA) is much less toxic to amphibians than Garlon 4 (triclopyr BEE). Garlon 3A is slightly to not acutely toxic in amphibians. Garlon 4 is moderately acutely toxic. Table E-7 in Appendix E and Table 4-9 summarize available amphibian toxicity studies.

For Garlon 3A, the 96-hour LC₅ and LC₅₀ values for the Frog Embryo Teratogenesis Assay¹⁰⁷ on *Xenopus laevis* (African clawed frog) are 119 and 162.5 mg a.e./L, respectively. The corresponding values for Garlon 4 were 6.7 and 9.3 mg a.e./L respectively.¹⁰⁸ No statistically significant increase in teratogenic effects were observed at sub-lethal concentrations.

In a study of *Rana pipiens* (leopard frog), *Rana clamitans* (green frog), and *Rana catesbeiana* (bullfrog), triclopyr acid reduced the response of amphibians to prodding.¹⁰⁹ Exposures to 0.6, 1.2, 2.4 and 4.8 mg a.e./L triclopyr acid caused no effect on hatching success or the incidence of malformations. However, all newly hatched tadpoles exhibited avoidance behavior of triclopyr-contaminated water. In leopard frog tadpoles, concentrations of 1.2, 2.4 and 4.8 mg a.e./L resulted in temporary dulled responsiveness or paralysis for 1, 3, and 5 days respectively. Newly hatched green frog and bullfrog tadpoles died when exposed to 2.4 or 4.6 mg a.e./L. For these two species, temporary decreased responsiveness lasted three days when tadpoles were exposed to 1.2 mg a.e./L.

In field studies in southwest Virginia, no significant difference in salamander abundance was noted after thin-line application of Garlon 4.¹¹⁰

Levels of concern for amphibians: The USFS reports neither exposure estimates nor TRVs for tadpoles or other amphibians. Since amphibian studies are available for triclopyr, we used them to estimate risk to amphibians. The only available acute study for triclopyr BEE produced an LC₅ of 6.7 mg a.e./L in a teratogenesis assay,¹⁰⁸ which we used as the acute TRV for the MMWD assessment.

For chronic exposures, we use the 1.2 mg/L LOEC for responsiveness to stimuli for triclopyr acid as the chronic TRV for the MMWD assessment. The paucity of data for amphibians increases the uncertainty of the risk estimates obtained using these TRVs.

Although we hypothesize that triclopyr TEA is less toxic, there is insufficient information. Therefore, the same acute and chronic TRVs are used for triclopyr TEA.

4.3.3.C Aquatic Invertebrates

The information available for aquatic invertebrate LC₅₀ values suggests that the sensitivity of most invertebrates to triclopyr is similar to that of fish, with triclopyr BEE being much more toxic than triclopyr acid or TEA salt. The most sensitive species were terrestrial insects with aquatic life stages such as dragonflies and mayflies.

In one study, *Daphnia magna* (water flea) adults were exposed to triclopyr TEA at concentrations of 57.9, 105, 204, 404, and 830 mg a.e./L for 21 days.¹¹¹ At the NOEC of 57.9 mg a.e./L, no significant effects were noted on mean number of broods, total young produced, mean number of young per brood or mean size of young. At the next higher concentration, 105 mg a.e./L, there was a statistically significant decrease in total young produced and mean number of young per brood. Table E-8 in Appendix E and Table 4-9 give a summary of the available triclopyr toxicity studies for aquatic invertebrates.

Triclopyr TEA is much less toxic than triclopyr BEE to estuarine and marine invertebrates. Table E-8 in Appendix E summarizes this information. The lowest LC₅₀ for triclopyr TEA for an estuarine invertebrate was 58 mg/L for an eastern oyster.¹¹² The LC₅₀ for the same species exposed to triclopyr BEE was 0.32 mg/L.¹¹³ The highest LC₅₀ values for triclopyr TEA and BEE respectively are >1,000 mg/L for fiddler crabs¹¹⁴ and 2.47 mg/L for estuarine shrimp.¹¹⁵ It is unclear whether these studies are reporting acid equivalents or active ingredient.

Terrestrial invertebrates with aquatic larvae, including Ephemeroptera (mayflies), Plecoptera (stoneflies), Trichoptera (caddisflies), and Odonata (dragonflies), were evaluated for sensitivity to Garlon 4 by exposure in a flow-through system for one hour, with mortality assessed at 48-hours.¹¹⁶ This exposure scenario mimics transient stream contamination from overspray. For most species, LC₅₀ values were greater than 290 mg/L; however, the trichopteran *Dolophilodes distinctus* showed high sensitivity in these tests, with LC₅₀ values averaging 0.6 (90% CI = 0.07–1.27) mg/L, and for one form of stonefly (*Pycnopsyche guttifer*), an LC₅₀ of 61.7 (90% CI = 21.8–126) mg/L was observed. The authors indicate that there was high mortality in the controls and presented the results with some caveats. A second study that did not appear to have these experimental difficulties indicated that exposure of *D. distinctus* to a concentration of 3.2 mg/L for one hour resulted in 35% mortality after 24 hours. An LC₅₀ of 4.45 mg/L was calculated for this study.

A 2007 study of the toxicity of TCP and chlorpyrifos (a pesticide that also degrades to form TCP) to *Daphnia carinata* found an acute LD₅₀ for TCP of 0.0002 mg/L.¹¹⁷ The toxicity of TCP to *D. carinata* was lower in natural water, and no effects were observed on *D. carinata* at concentrations of 0.002 mg/L. This value is not a NOEC, since other concentrations were not tested.

Levels of concern for aquatic invertebrates: The USFS uses an acute LC₅₀ for triclopyr BEE of 8.55 mg/L observed for *Ameletus sp.* for the acute TRV.¹¹⁸ A value of 12 mg/L is used by EPA. We use the LC₅₀ value of 4.45 mg/L observed for a 1-hour exposure of *D. distinctus* and divide by six to account for the absence of a NOEC. The resulting acute TRV for triclopyr BEE is 0.74 mg/L. The acute TRV for triclopyr TEA used by the USFS is the 80.7 mg/L NOEC for *Daphnia*. In the MMWD risk assessment, we used the LC₅₀ value of 58 mg/L for the eastern oyster and divided by six to account for the lack of a NOEC to give a TRV of 9.67.

For chronic toxicity of both the BEE and the TEA salt, the USFS uses EPA's acute NOEC of 80.7 mg/L for triclopyr acid, since the BEE degrades rapidly to the acid. However, in the time frame of the MMWD long-term runoff scenario, triclopyr acid degrades primarily to TCP, thus we estimated risk based on TCP, not triclopyr acid. There are no studies on the chronic toxicity of TCP to invertebrates, just the acute study in which no effects on *D. carinata* were found at a

concentration of 0.002 mg/L in natural waters. This study did not define a NOEC. In the absence of any other data, we used the acute LC₅₀ of 1.5 mg/L for trout exposed to TCP and divided by six to account for the absence of a NOEC to give 0.25 as the chronic TRV for aquatic invertebrates for the MMWD assessment

4.3.3.D Aquatic Plants

Triclopyr formulations range from slightly to highly toxic to aquatic plants. Based on EC₅₀ values, triclopyr TEA is about equally toxic to algae (lowest EC₅₀ of 4.2 mg a.e./L) and aquatic macrophytes (lowest EC₅₀ of 6.2 mg a.e./L). Triclopyr BEE is more toxic than the TEA salt, with EC₅₀ values as low as 0.074 mg/L for algae and 0.65 mg/L for macrophytes. At 2.6 mg/L triclopyr acid, there is inhibition of carbon fixation.¹¹⁸ A chronic toxicity study reports a NOEC for Garlon 3A of 0.08 ppm on cell density in the green alga *Ankistrodesmus* sp.¹¹⁹ Eurasian watermilfoil, an invasive aquatic macrophyte, is not controlled by concentrations of Garlon 3A of 0.25-2.5 mg a.e./L at exposure periods less than 6 hours.¹²⁰ However, treatment for 72 hours at 0.25 mg/L was very effective at controlling watermilfoil.

Levels of concern for aquatic plants: The USFS uses an EC₅₀ value of 0.07 mg a.e./L for algae as the TRV for triclopyr BEE for aquatic plants. For triclopyr TEA, the USFS/SERA uses a TRV of 4.2 mg ae/L. We also use these values in the MMWD risk assessment.

4.3.4 Data Gaps

Most of the literature cited in USFS 2003 and in the EPA's Terretox database come from the re-registration decision for triclopyr. Before a chemical can be reregistered, the EPA requires: acute toxicity tests for mammals (as part of the human risk assessment), birds, fish, honeybees, and aquatic invertebrates; reproductive toxicity for birds; chronic toxicity tests for mammals; and very minimal chronic toxicity tests for fish, birds and aquatic invertebrates.

Acute toxicity information was available for representative surrogate species for all nine wildlife taxa, with substantial variability in sensitivity to triclopyr observed. More information describing this variability would better define the range of toxicity. LOELs were available for the sub-lethal effects of triclopyr for at least one surrogate species. Some sub-lethal toxicity information was available for selected taxa. More chronic toxicity information for all taxa would help to clarify possible sub-lethal effects. There were no data on the neurotoxicity or endocrine disrupting ability of triclopyr or its formulated products, and there were no studies for insects other than honeybees.

Field measurements of the effects of triclopyr in natural settings are rare. More field studies would help clarify the differences between laboratory and field toxicity of triclopyr.

Other good targets for future research include: sub-lethal toxicity studies (specifically endocrine disruption at sub-lethal concentrations), comprehensive field measurements of triclopyr residue concentrations on vegetation and in surface waters near application sites, and whole-ecosystem effects due to triclopyr exposure.

Table 4-8: Comparison of Triclopyr Toxicity Reference Values Used in USFS and MMWD Risk Assessments

		USFS			MMWD				
Taxa	Exposure Type	Selected Endpoint	Dose	Adjustments to Dose	TRV Used in USFS Risk Assessment	Selected Endpoint	Dose	Adjustments to Dose	TRV Used in MMWD Risk Assessment
Humans – Triclopyr BEE and TEA									
	acute RfD, male	NOAEL (rat)	100 mg/kg-day	÷100 ^a	1 mg/kg-day	NOAEL (rat)	100 mg/kg-day	÷100 ^a	1 mg/kg-day
	acute RfD, female	NOAEL (rat)	5 mg/kg-day	÷100 ^a	0.05 mg/kg-day	NOAEL (rat)	5 mg/kg-day	÷100 ^a	0.05 mg/kg-day
	chronic RfD, female	NOAEL (rat)	5 mg/kg-day	÷100 ^a	0.05 mg/kg-day	NOAEL (dog)	12 mg/kg-day (TCP)	÷1000 ^b	0.012 mg/kg-day
	chronic RfD, male	NOAEL (rat)	5 mg/kg-day	÷100 ^a	0.05 mg/kg-day	NOAEL (rat)	5 mg/kg-day (triclopyr)	÷100 ^a	0.05 mg/kg-day
Mammals – Triclopyr BEE and TEA									
	acute	NOAEL (rat)	100 mg/kg-day	None	100 mg/kg-day	NOAEL (rat)	100 mg/kg-day	None	100 mg/kg-day
	chronic	NOAEL (rat)	5 mg/kg-day	None	5 mg/kg-day	NOAEL (rat)	5 mg/kg-day	None	5 mg/kg-day
Birds – Triclopyr BEE and TEA									
	acute	LC ₅₀ (BEE, bobwhite)	3,880 mg/kg-day	X 10% ^c	388 ^b mg/kg-day	LC ₅₀ (BEE, bobwhite)	3,880 mg/kg-day	X 10% ^c ÷6 ^d	65 ^c mg/kg-day
	chronic	NOEC (acid, mallard)	100 mg/kg-day	X 10% ^c	10 mg/kg-day	NOEC (acid, mallard) ^c	100 mg/kg-day	X 10% ^c	10 mg/kg-day
Insects – Triclopyr BEE and TEA									
	honeybees	LC ₅₀	>100 (µg/bee)	÷0.000093 ^e	1,075 mg/kg-day	LC ₅₀	>100 (µg/bee)	÷0.000093 ^e ÷6 ^e	179 mg/kg-day
Plants – Triclopyr BEE									
	vegetative vigor	NOEC (BEE, sunflower)	0.0039 lb/acre	None	0.0039 lb/acre	NOEC (BEE, sunflower)	0.0039 lb/acre	None	0.0039 lb/acre
	seed emergence	EC ₅₀ (BEE, onion)	0.003 lb/acre	None	0.003 lb/acre	EC ₅₀ (BEE, onion)	0.003 lb/acre	None	0.003 lb/acre
Plants – Triclopyr TEA									
	vegetative vigor	NOEC (BEE, sunflower)	0.0041 lb/acre	None	0.0041 lb/acre	NOEC (BEE, sunflower)	0.0041 lb/acre	None	0.0041 lb/acre
	seed emergence	EC ₅₀ (BEE, onion)	0.333 lb/acre	None	0.333 lb/acre	EC ₅₀ (BEE, onion)	0.333 lb/acre	None	0.333 lb/acre
Fish – Triclopyr BEE									
	acute	LC ₅₀ (BEE, bluegill)	0.25 mg/L	None	0.25 mg/L	LC ₅₀ (BEE, bluegill)	0.25 mg/L	÷20 ^c	0.013 mg/L
	chronic	NOEC (TEA, fathead minnow)	104 mg/L	None	104 mg/L	LC ₅₀ (TCP, trout)	1.5 mg/L	÷20 ^c	0.075 mg/L

Table 4-8 (cont.): Comparison of Triclopyr Toxicity Reference Values Used in USFS and MMWD Risk Assessments

		USFS			MMWD				
Taxa	Exposure Type	Selected Endpoint	Dose	Adjustments to Dose	TRV Used in USFS Risk Assessment	Selected Endpoint	Dose	Adjustments to Dose	TRV Used in MMWD Risk Assessment
Fish – Triclopyr TEA									
	acute	LC ₅₀ (TEA, bluegill)	199 mg/L	None	199 mg/L	NOEC (TEA, fathead minnow)	104 mg/L	None	104 mg/L
	chronic	NOEC (TEA, fathead minnow)	104 mg/L	None	104 mg/L	LC ₅₀ (TCP, trout)	1.5 mg/L	÷20 ^d	0.075 mg/L
Amphibians – Triclopyr BEE and TEA									
	acute	NE	NE	NE	NE	NOEC (BEE, tadpoles)	6.7 mg/L	None	6.7 mg/L
	chronic	NE	NE	NE	NE	LOEC (BEE, tadpoles)	1.2 mg/L	None	1.2 mg/L
Aquatic Invertebrates – Triclopyr BEE									
	acute	LC ₅₀ (mayfly)	8.55 mg/L	None	8.55 mg/L	LC ₅₀ (<i>D. distinctus</i>)	4.45 mg/L	÷6 ^d	0.74 mg/L
	chronic	NOEC (Daphnia)	80.7 mg/L	None	80.7 mg/L	LC ₅₀ (TCP, trout)	1.5 mg/L	÷6 ^d	0.25 mg/L
Aquatic Invertebrates – Triclopyr TEA									
	acute	LC ₅₀ (mayfly)	132.9 mg/L	None	132.9 mg/L	LC ₅₀ (oyster)	58 mg/L	÷6 ^d	9.67 mg/L
	chronic	NOEC (Daphnia)	80.7 mg/L	None	80.7 mg/L	LC ₅₀ (TCP, trout)	1.5 mg/L	None	0.25 mg/L
Aquatic Plants – Triclopyr BEE									
	algae	EC ₅₀ (algae)	0.07 mg/L	None	0.07 mg/L	EC ₅₀ (algae)	0.07 mg/L	None	0.07 mg/L
	macrophytes	EC ₅₀ (algae)	0.07 mg/L	None	0.07 mg/L	EC ₅₀ (algae)	0.07 mg/L	None	0.07 mg/L
Aquatic Plants – Triclopyr TEA									
	algae	EC ₅₀ (algae)	4.2 mg/L	None	4.2 mg/L	EC ₅₀ (algae)	4.2 mg/L	None	4.2 mg/L
	macrophytes	EC ₅₀ (algae)	4.2 mg/L	None	4.2 mg/L	EC ₅₀ (algae)	4.2 mg/L	None	4.2 mg/L

NE = not evaluated.

^a The animal NOAEL was divided by an interspecies uncertainty factor of 10 and an intraspecies factor of 10, equivalent to dividing by 100. This is EPA's RfD.

^b The animal NOAEL for TCP was used as the endpoint and was divided by an interspecies uncertainty factor of 10, an intraspecies factor of 10, and an FQPA factor of 10, equivalent to dividing by 1000. This is EPA's PAD. See Section 4.2.1 for more discussion.

^c The dietary LC₅₀ was multiplied by 10%, which is the USFS estimate of the percentage of a bird's body weight it eats per day, in order to calculate dose in mg/kg bw.

^d The factor of six or 20 is used when there is only an LD₅₀ or LC₅₀ value available, instead of a NOAEL or NOEC, because the endpoint of killing 50% of the organisms is not acceptable in most cases. The factor of six is used by the US EPA in evaluation of endangered species effects and is based on a review of literature studies in which both LD₅₀ or LC₅₀ and NOAEL or NOEC values were available for comparison. The factor of 20 is used for especially sensitive species such as salmonids. See text on page 4-7 for more discussion of this concept.

^e The LC₅₀ of 100 µg/bee was converted to a dose in mg/kg by multiplying by the conversion factor between mg and µg (0.0001 mg/µg) and dividing by the USFS estimate of body weight of a bee: 0.000093 kg.

Table 4-9: Summary of Triclopyr Ecotoxicity Data from AQUIRE database

Taxa	Endpoint	Formulation ^a	Number of Studies	Dose (mg/kg, or mg/L for aquatic) ^b		
				Min	Median	Max
Birds	8-day LC ₅₀	TEA	2	>4,660	^c	>5,380
	8-day LC ₅₀	acid	3	2,930	3,270	5,620
	14-day LD ₅₀	acid	2	1,480	^c	1,700
	8-day LC ₅₀	BEE	4	3,740	4890 ^d	>6,700
	21 and 14-day LD ₅₀ ^e	BEE	2	510	^c	610
	5-day LD ₅₀	Garlon 4	1	^g	1,920	^g
	LOEC–reproductive & weight changes	Garlon 4 & acid	3	200 (acid)	500 (G4)	500 (acid)
	NOEC–reproductive & weight changes	Garlon 4 & acid	3	100 (acid)	150 (G4)	500 (acid)
Honeybees	1-7 day LD ₅₀ ^e	NR	3	>25	>100 µg/bee	>100
Fish	1-4 day LC ₅₀ ^e	Garlon 3	21	188	249	351
	1-4 day LC ₅₀ ^e	Garlon 4	31	0.59	1.56	26
	1-4 day LC ₅₀ ^e	TEA	7	83	176	441
	1-4 day LC ₅₀ ^e	acid	26	5.3	8.15	148
	1-4 day LC ₅₀ ^e	BEE	37	0.22	0.74	1.67
	10-24 hour LOEC–behavior, avoidance ^e	Garlon 3	2	141	^c	564
	10-24 hour LOEC–behavior, avoidance ^e	Garlon 4	2	0.45	^c	14.2
	LOEC–developmental	TEA	3	114	<162	178
NOEC–stunted growth	TEA	1	^f	<104	^f	
Amphibians	4-day LC ₅₀	Garlon 3	1	^f	162	^f
	4-day LC ₅₀	Garlon 4	1	^f	9.3	^f
	2-day LC ₁₀₀	acid	2	2.4	^d	2.4
	LOEC–responsiveness	acid	3	1.2	1.2	2.4
Aquatic Invertebrate	LC ₅₀	BEE	7	0.32	1.3	8.9
	LC ₅₀	BEE ^g	13	0.17	320	370
	LC ₅₀	TEA	7	>56	326	1,055
	LOEC–brood size	TEA	1	^f	57	^f
	NOEC–brood size	TEA	1	^f	29	^f

See Appendix E for more details on the studies reported here.

^a Different salts or esters of triclopyr are used in the toxicity studies. The “Formulation” column notes the active ingredient and/or product used to obtain the endpoint in the Dose column. Products and active ingredients are abbreviated as follows: TEA = triethylamine salt; BEE = butoxyethyl ester; acid = triclopyr acid; and NR = not reported. The active ingredient in Garlon 3 is triclopyr TEA and the active ingredient in Garlon 4 is triclopyr BEE. The abbreviations in the parentheses in the Dose column are: G4 = Garlon 4 and G3 = Garlon 3.

^b All aquatic toxicity is reported in mg/L. All terrestrial toxicity (except insects) is reported in mg/kg. Insect toxicity are reported in either µg/bee for honeybees or kg/ha for all other insects.

^c No median is reported because there were only two studies.

^d Averaged from two values: 3,740 and 6,040 mg/kg.

^e Different study durations (8 versus 21 days) are grouped. See Appendix E for specifics.

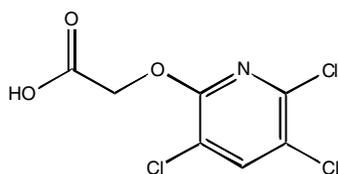
^f Only one value was reported.

^g The AQUIRE database states that a formulated product of triclopyr BEE was used (e.g. Garlon 4), however, the exact product is not reported.

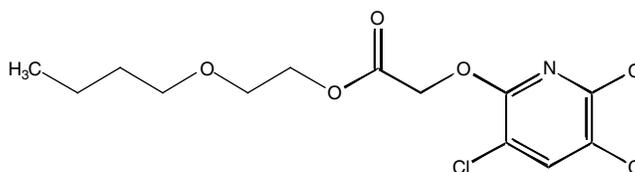
4.4 Environmental Fate of Triclopyr

4.4.1 Overview

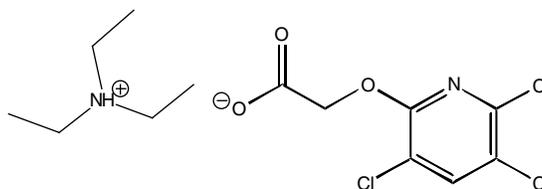
Triclopyr acid (CAS number 55335-06-3) is a chloropyridinyl herbicide, with empirical formula of $C_7H_4Cl_3NO_3$. The chemical structure is shown below. Triclopyr is usually formulated as an amine salt or as an ester of the carboxylic acid; the Garlon 4 Ultra product selected for consideration by MMWD contains the butoxyethyl ester of triclopyr (CAS number 64700-56-7). Once in an aqueous environment, esters of triclopyr hydrolyze fairly rapidly and react similarly to triclopyr itself, thus studies of both triclopyr and triclopyr salts and esters are reviewed. Table 4-10 summarizes the chemical and physical properties of triclopyr.



Triclopyr acid



Triclopyr butoxyethyl ester



Triclopyr triethylamine salt

Triclopyr is a weak organic acid, with pK_a of 2.93.⁹⁵ In a saturated aqueous solution of triclopyr (concentration of 430 mg/L), the acid is almost completely dissociated to form the triclopyr anion and acid (H_3O^+). The pH of this solution is quite acidic, at 2.77.

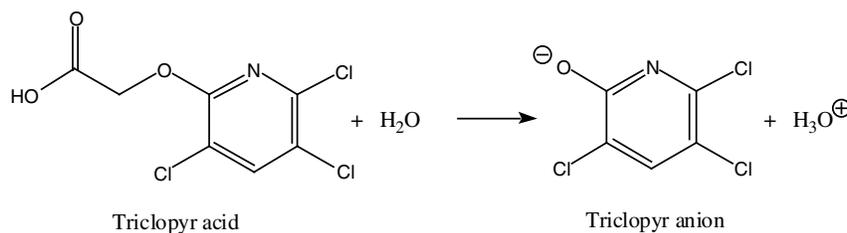


Table 4-10: Chemical and Physical Properties of Triclopyr

Property	Triclopyr acid	Triclopyr TEA	Triclopyr BEE	TCP
CAS number	55335-06-3	57213-69-1	64700-56-7	6515-38-4
EPA PC code	116001	116002	116004	206900
Molecular weight (g/mol)	256.5	357.6	356.7	198.6
Water solubility (mg/L at ~25°)	430	234,000	6.8	44,000
Half-life (days)				(pH 7) 12–229
Hydrolysis	--	--	0.5 (pH 6.7)	270
Anaerobic	1,600	1,600	26.4	--
Aerobic	12.8	12.8	--	129 (10°C)
Field dissipation	139	139	39	8–96
Vapor pressure (mm Hg at ~25°C)	1.26×10^{-6}	$< 1 \times 10^{-8}$	3.6×10^{-6}	
K_{oc} (mL/g)	19–78	24–144	6,000	14–86
K_{ow}	0.205	1.23	1.2×10^4	--
K_H (atm·m ³ /mol at ~25°C)	9.65×10^{-10}	6.0×10^{-7}	2.47×10^{-7}	--

Data source: References 9, 95, and 121.

4.4.2 Water Solubility and Soil Binding of Triclopyr

The parent acid triclopyr is a solid at room temperature and has moderate water solubility (430 mg/L at 25°C). The TEA salt of triclopyr has much higher water solubility (234,000 mg/L at 25°C) and the BEE derivative is relatively insoluble (6.81 mg/L at 25°C). The octanol-water partition coefficient, K_{ow} , for triclopyr BEE is 1.2×10^4 indicating low solubility in water relative to organic solvents and some potential for bioaccumulation, although because the half-life of triclopyr BEE is quite short, bioaccumulation is unlikely to occur to a significant extent. The K_{ow} for triclopyr TEA is much lower at 1.23, indicating low potential for bioaccumulation.

The organic-carbon-adjusted soil adsorption coefficient (K_{oc}) of triclopyr acid is 19–78 mL/g, a value that indicates that, in a mix of soil and water, most triclopyr remains dissolved in water rather than bound to organic matter in soil. This property makes triclopyr acid mobile in soils. Triclopyr BEE has a much higher K_{oc} at 6,000 cm³/g; it adsorbs to plants in aqueous systems and organic matter in soils, but is rapidly transformed to the acid.

4.4.3 Persistence of Triclopyr

Triclopyr BEE degrades rapidly in both water and soil to triclopyr acid, with a half-life of approximately 0.5 days in water and 3 hours in soil, with hydrolysis rates increasing at higher pH. In water, both hydrolysis and photolysis contribute to the degradation process. In soils, microbial activity contributes to the degradation process, with rate increases observed when temperature and moisture content of the soil are high. The TEA salt dissolves to form the salt of the acid. Triclopyr acid is stable to hydrolysis, with photolysis the primary route of degradation in water. Photolysis does not contribute significantly to degradation in soils.

Triclopyr acid degrades to form 3,5,6-trichloro-2-pyridinol (TCP) and 3,5,6-trichloro-2-methoxypyridine (TMP) under aerobic conditions. In a lab soil-column study, the relative amounts of these products at 54 days were 4% triclopyr, 88% TCP, and 15% TMP for triclopyr acid-treated soil. For triclopyr BEE-treated soils, concentrations were 6% triclopyr, 88% TCP

and 7%TMP.⁹⁶ Triclopyr acid and TCP are both moderately persistent in the environment. On average, the half-life of triclopyr acid is 11–100 days in temperate climates; in cold climates, half-lives range from 365–720 days (see Table 4-11). The transformation products TCP and TMP are more persistent, with half-lives of 12–229 days for TCP and 50–450 days for TMP.⁹⁵ Table 4-10 provides half-lives for specific studies under a variety of different conditions, and some of the more relevant studies are summarized briefly below.

The dissipation half-life of triclopyr in water is less than a laboratory-measured half-life. In a recent study by the San Francisco Estuary Institute, a creek was treated with triclopyr TEA.¹²² During the hours following the application, triclopyr concentrations were measured at 6.65–250 µg/L, below the TRVs for several reference species. Several days after the application, the concentration was 12 µg/L. Another study evaluated the fate of triclopyr BEE in streams by directly injecting triclopyr BEE into a stream at a concentration equivalent to an application rate of 3.6 lb a.i./acre.¹²³ The highest concentrations of triclopyr BEE were found in leaf packs of degraded hardwood foliage that had been placed in the stream. Within hours, triclopyr BEE in the water had degraded to triclopyr acid; degradation in the leaf packs was slower. Residues of triclopyr acid in the sediments were ten times lower than those in the water, but remained longer.

Compared to aqueous half-lives, soil dissipation half-lives of triclopyr are substantially longer, (see Table 4-10). For many of these studies, only triclopyr residues were monitored, and the primary degradation product TCP was not measured. The National Marine Fisheries Service (NMFS) released a Biological Opinion in November 2008 for salmonid exposure to several organophosphorus pesticides and their degradation products, one of which is TCP. The NMFS noted that substantial amounts of TCP remain in the environment at 365 days post-application, leaving substantial amounts available for runoff. The solubility and K_{oc} values are similar between triclopyr and TCP, indicating that runoff potential is similar for the two compounds.¹²⁴

Table 4-11: Half-Life of Triclopyr Acid, Butoxyethyl Ester (BEE), and Triethylamine Salt (TEA)

Conditions	Half-Life (days)	Type of Half-Life	Comments	Reference
Water: Triclopyr acid				
Laboratory	142	Aerobic	Does not adsorb to suspended solids or organic matter	125
Laboratory	Stable	Hydrolysis	Acid is stable with respect to hydrolysis	126
	4.7 mos	Aerobic dissipation	Degradation to TCP	127
Anaerobic	3.5 years	Anaerobic dissipation	Degradation to TCP	128, 129
Lab	270	Hydrolysis		130
Natural water	1.3	Photolysis		131
Water: Triclopyr triethylamine salt				
Natural water, 25°C, pH 6.7	0.5	Hydrolysis	TEA dissolves to form the acid.	132
River water, 25°C, pH 8.5	0.713	Photolysis	Hydrolysis half -life	133
Buffer solution, 25°C, pH 7	0.357	Photolysis	Hydrolysis half -life	133
Whole pond application in CA, MS, and TX:		Field dissipation	Dissipation of triclopyr and metabolites is similar in the different states.	134
In water	5.9-7.5			
In sediment	2.8-4.6			
Water: Triclopyr BEE				
Laboratory: 15°C, pH 5	209	Hydrolysis		133
Laboratory: 25°C, pH 5	165	Hydrolysis		133
Laboratory: 25°C, pH 5	84	Hydrolysis		133
Laboratory: 25°C, pH 5	84	Hydrolysis		133
Laboratory: 35°C, pH 5	25.9	Hydrolysis		133

Table 4-11 (cont.): Half-Life of Triclopyr Acid, Butoxyethyl Ester (BEE), and Triethylamine Salt (TEA)

Conditions	Half-Life (days)	Type of Half-Life	Comments	Reference
Soil: Triclopyr acid				
Reported range in soil	12-27			130
Cold climate	365-730			135
Silty clay loam	8	Aerobic		125, 126
Silt loam	18			
Anaerobic conditions	1,300	Anaerobic		125
Aerobic conditions	32	Aerobic	Average	126
Silt-loam	69	Aerobic		126
MS	43	Field dissipation		126
CA, grass	36	Field dissipation		126
CA, bare soil	35	Field dissipation		126
Nova Scotia	15	Field dissipation		126
Ontario	26	Field dissipation		126
Soil: Triclopyr BEE				
Not reported	3 h	Aerobic hydrolysis to acid		136
Not reported	1	Anaerobic hydrolysis to acid		136
Not reported	26.45	Anaerobic		137
Not reported	39	Field dissipation		137
Gorse and pasture grass	107	Field dissipation	Soil sampled from sheltered sites beneath bushes	138
Gorse and pasture grass	97	Field dissipation	Soil from exposed sites at least 3m away from bushes	138
Clear-cut site in both exposed & unexposed soil	96.0 ± 9.9	Field dissipation	Average value. Half-life in unexposed soil was less than half-life in exposed soil	139
Forest sites (soil and litter): Right of way in Ontario, Canada (soil and grass):	10	Field dissipation		140
Southwest OR	11-25	Field dissipation		141
25°C, pH 5.7, sandy loam	<0.5	Anaerobic		142
25°C, pH 6.3, sandy loam	88.6	Anaerobic		133
25°C, pH 5.3, loam	39	Field dissipation		133
25°C, pH 5.7, sandy loam	16.2	Anaerobic		133
25°C, pH 6.3, sandy loam	63.8	Anaerobic		133
Soil: Triclopyr, TEA salt				
Southwest OR	11-25	Field dissipation		141
	12.8	Aerobic		137
	139	Field dissipation		137
	1,600	Anaerobic		137
25°C, pH 6.6, silty loam	17.7	Aerobic		133
25°C, pH 5.2, silty clay	7.8	Aerobic		133
25°C, pH 5.7, sandy loam	1,300	Anaerobic		133
23°C, pH 7.5, loam	85.3	Soil		133
25°C, pH 6.3, sandy loam	1,900	Anaerobic		133
Air: Triclopyr acid				
	>12 hr	Photolysis	Exists in both vapor and particulate phase	125
	3.3		Reacts with hydroxyl radicals	125

Triclopyr can be transported away from an application site or degrade in soil, water and air through a number of different chemical or biological processes. The most important processes for dissipation of triclopyr are microbial biodegradation, runoff into surface waters, uptake by plants, and photodegradation in water. Figure 4-1 describes the various degradation pathways for triclopyr.

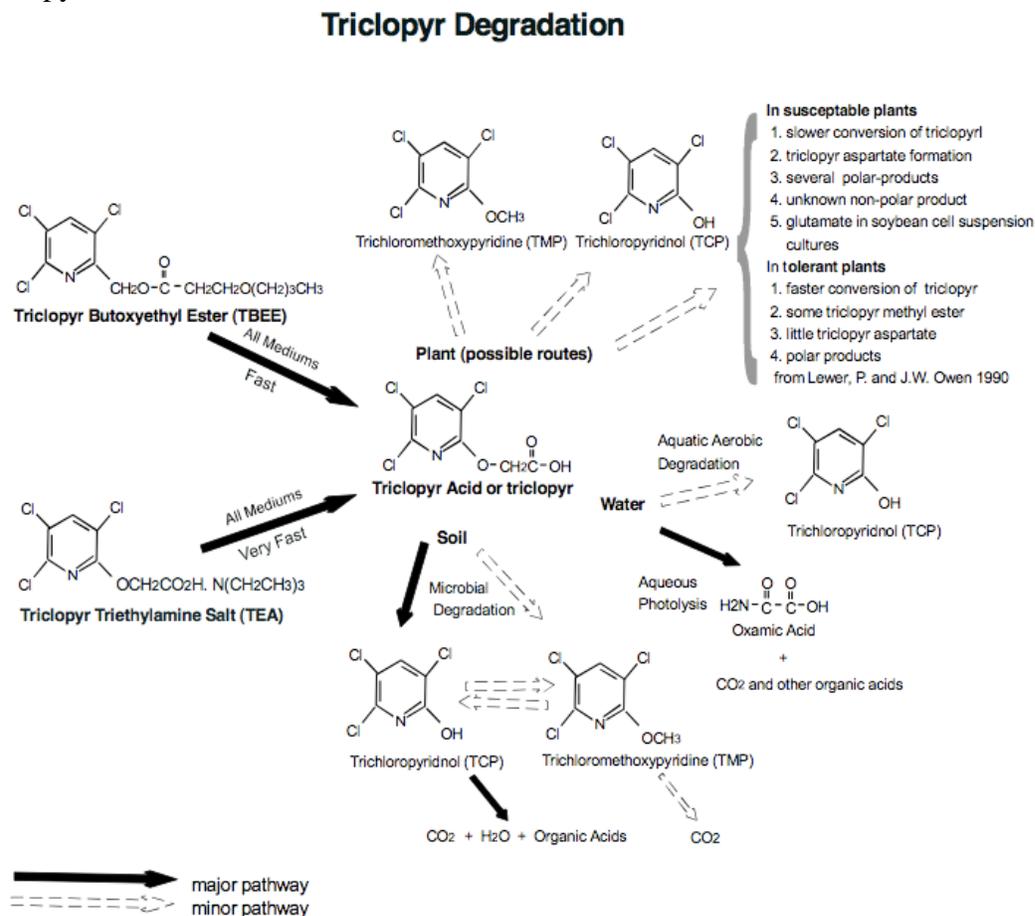


Figure 4-1: Degradation pathways for triclopyr. (Schematic excerpted from reference 95).

4.4.3.A Microbial Degradation

The primary route of triclopyr degradation in the environment is via microbial degradation in soil.⁹⁵ Under aerobic conditions, 3,5,6-trichloropyridinol (TCP) is the primary degradation product. Further degradation yields carbon dioxide, water and organic acids. Microbial activity increases with higher temperatures and moisture levels. TCP degrades more slowly than triclopyr and is similarly water soluble.

4.4.3.B Transport by Air

Air transport of triclopyr away from the application site can occur through spray drift during and for a short time after an application. Spray drift can contaminate soil and surface waters, damage non-target plants, and expose humans and wildlife through inhalation and dermal exposure. Damage to plants from off-target movement of triclopyr can be significant.¹⁴³ Post-application volatilization drift is not a significant source of off-site transport for triclopyr acid or BEE because of their low vapor pressures (1.26×10^{-6} mm Hg and 3.6×10^{-7} , respectively at 25°C),

although volatilization can still contribute significantly to toxicity to non-target plants, even at the low concentrations anticipated from volatilization. Similar effects have been observed for the herbicide propanil (vapor pressure = 6.4×10^{-7} mm Hg at 25°C), resulting in restrictions on its use in California during certain times of the year because of damage to prune trees.¹⁴⁴

When dissolved in water, triclopyr TEA or BEE do not appreciably escape to the air, as indicated by their very low Henry's law constants of 9.65×10^{-10} atm-m³/mol and 2.47×10^{-7} atm-m³/mol, respectively.

4.4.3.C Transport by Water

Triclopyr acid and TEA salt are considered to be mobile in soils because of their low K_{oc} values and high water solubility. Triclopyr BEE is less mobile, but rapidly breaks down to form triclopyr acid. Triclopyr sorption to soils seems to increase with time, decreasing its mobility.¹⁴⁵ In laboratory studies of soil leaching, little downward mobility of triclopyr was noted, and most of the applied herbicide stayed in the top 10 cm of soil.¹⁴⁶ Triclopyr runoff from soil surfaces was also not found to be a major contributor to surface water contamination, with runoff samples containing less than 1 µg/L triclopyr from one to 105 days after treatment at 2.7 lbs a.i./acre.¹⁴⁷ The breakdown products appear to be relatively immobile as well.¹⁴⁸ Most of the TCP is expected to stay in the top one to two inches of soil.¹⁴⁹

Other work indicates that there are conditions where substantial leaching of relatively immobile herbicides to groundwater occurs—when soil quality is poor, containing a high percentage of gravel and a low organic matter,¹⁵⁰ or in the presence of fractured soils.¹⁵¹

Although most of the field studies designed to measure triclopyr water contamination indicate that triclopyr will not run off in substantial amounts, actual monitoring data indicate that triclopyr contamination of waterways is occurring. USGS water sampling through the National Water Quality Assessment Program (NAWQA) found that nationally, 6.4% of 4,435 surface water samples tested positive for triclopyr.²¹ In Oregon, where triclopyr is used more heavily in forestry applications, 47% of the 139 samples contained detectable triclopyr, with a maximum concentration of 2.87 µg/L. In California, where triclopyr is used on flooded rice fields that drain to surface waters, the maximum level detected is slightly higher at 3.35 µg/L, and 11.5% of 227 samples contained detectable triclopyr. Since the NAWQA monitoring program is not targeted at specific applications or storm events, it is unlikely that a true maximum concentration was observed.

4.4.3.D Uptake by Plants

Plants treated with triclopyr absorb the chemical through foliage, roots or cut stems of a plant. Foliar uptake is rapid, with 90% of applied triclopyr taken up within 12 hours.⁹⁵ Surfactants increase the rate of uptake from foliage and stems. While root uptake is possible, foliar sprays are more effective for herbicidal treatments.

Triclopyr residues can persist in dead plant stems. In one study, levels of triclopyr up to 0.9 ppm were detected in dead stems after 22–26 months.¹⁵² Another study evaluated triclopyr residues in animal feed.¹⁵³ One year after treatment, residues ranging from 0.2–6.7 ppm were measured. It was estimated that residues decreased by 42% in six days, 72% after 28 days and 98% after 365

days. Two similar studies by Dow¹⁵⁴ gave similar results, with estimated half-lives on vegetation of four to ten days. TCP was also measured, with the highest levels at 20 ppm, decreasing to non-detects. Overall, dissipation of triclopyr from plant tissue is slower than dissipation in soils. There is also reason to believe that foliar dissipation of triclopyr is longer than glyphosate. A comparison of glyphosate and triclopyr residues in sugar maple (*Acer saccharum*) foliage suggests that triclopyr acid persists longer (90% dissipation in 33 days) than glyphosate (90% dissipation in 16 days). Dissipation of these pesticides from dead foliage was not explicitly discussed.

4.4.3.E Field Studies on the Environmental Fate of Triclopyr

A number of field studies have been conducted on the environmental fate of triclopyr. Those most relevant to the MMWD site are reviewed here. Summaries of additional studies can be found in references 5 and 95.

Fate in soils: One study commissioned by Dow has relevant information to application on MMWD lands.¹⁵⁵ A clear-cut forestry site was treated with triclopyr BEE at 6.0 lb a.i./acre by helicopter, using buffer zones around the stream. Vegetation and soil samples were collected over time and analyzed for triclopyr, TCP and TMP. Only small quantities of the breakdown products were detected, compared with triclopyr. In one plot, TCP and TMP concentrations were about 0.57 and 0.29 percent of the triclopyr BEE applied, respectively. The half-life of triclopyr in vegetation was determined to be 15±9 days. The dissipation half-life of triclopyr in litter was determined to be 20±6 days. Data collected from soil samples indicated that triclopyr remained mainly in the top 6 inches of soil. Even in the exposed soil areas, which represent a worst case scenario, only a fraction of the percent applied was detected at soil intervals below 24 inches at six months after treatment. The average soil half-life for triclopyr was 96.0±9.9 days. The half-life of triclopyr in unexposed soil was shorter than in exposed soil.

Another study provided information on triclopyr concentrations in soil, vegetation and litter after an application of both triclopyr TEA and BEE to brush in Southwest Oregon at 2.0–3.9 lb a.i./acre for the salt and 1.5–2.9 lb a.i./acre for the ester.¹⁵⁶ At 37 days after application, 24 to 51% of the applied triclopyr was present in the surface soil. The soil was dry, as no rain had occurred during that period. From 37 to 79 days, the largest decrease in soil residues occurred. This coincided with a warm, moist period when the half-life ranged from 11 to 25 days. The herbicide concentration decreased more slowly during the winter. In the spring, the decrease in residues resumed, due to increased soil temperatures and microbial activity. The researchers found that triclopyr was practically immobile in soil-water and therefore would only move a short distance in forest subsurface flow. The half-life in litter was 31–59 days. TCP and TMP levels were not reported.

In a 1991 New Zealand study triclopyr levels were measured in stream runoff after an application to gorse and pasture grass treated with 3.5 lb a.i./acre of triclopyr BEE.¹⁵⁷ Samples were collected continuously for six months after treatment. The highest concentration of triclopyr was detected on the third sampling event following the first major rainstorm since the application at 41 to 46 days after treatment. Samples collected after that time yielded no detections, suggesting that the first substantial rainfall caused runoff of most of the available triclopyr. The total mass of the triclopyr in the stream water was calculated to be about 103 g or

equal to about 2.9% of the total triclopyr applied. TCP was not measured in this experiment. Adsorption of triclopyr to stream sediments and uptake by aquatic plants may have removed some of the herbicide from the water, suggesting that actual runoff rates might be higher. Triclopyr was not detected 400 m downstream of the sampling point. Soil samples from the treated site were also analyzed; half-lives of 107 days in sheltered sites and 97 days in exposed sites were determined. The researchers also noted that soil temperature and the amount and type of organic matter affect the persistence of triclopyr.

A 2008 California study evaluated the persistence of triclopyr from basal bark treatments of wild fig trees.¹⁵⁸ Trees were treated with 25% Garlon 4, an application rate that exceeded the labeled maximum use rate. No quantitative data or climate information were provided, but the authors noted that soil near the fig trunks contained high levels of triclopyr after five months. Mortality of native plants transplanted into treated sites was higher than that observed for control sites.

Region 5 (Pacific Southwest) of the USFS has conducted water quality monitoring after herbicide use in reforestation or invasive plant management in the Eldorado and Stanislaus National Forests between 1991 and 1999.¹⁵⁹ Triclopyr was monitored in five of these studies, both immediately after application to detect any spray drift into waterways and during the first runoff event, typically 60–90 days after the application. A buffer zone of at least 10 feet between streams and waterways was utilized, except for ephemeral streams. Out of 43 total water and sediment samples taken for the eight projects, 13 detections of triclopyr were noted, 12 less than 10 µg/L and one sample at 82 µg/L. The presence of triclopyr in the waterways was attributed to an insufficient buffer zone (less than 20 feet) during the applications. The degradates TCP and TMP were not analyzed.

Fate in lentic systems: A 2002 study in Minnesota tracked the fate of triclopyr applied directly to the shallow (1-2 m) part of a lake, using a red dye as a tracer.¹⁶⁰ Exact concentrations of triclopyr were not reported, but extrapolation from plots of the data indicate that triclopyr concentrations decreased from just less than 4.0 mg/L after the application to less than 0.1 mg/L 14 days later. Levels of TCP were also measured and found to be approximately 0.021 mg/L at the start of the application, declining to approximately 0.001 mg/L by day 21. The researchers explained the high TCP levels at the start of the application by noting that some TCP is present in triclopyr products. Another interesting observation made in this study was that the concentration of triclopyr in the surface layer of a lake where just the surface was treated (mimicking a helicopter or direct spray application, instead of an injection) was seven times higher than that in the deeper water, and concentration did not become uniform until five days after the application. The experimental section did not specify the sampling depth.

A 1996 Dow study evaluated triclopyr, TCP and TMP dissipation rates in water, sediments and fish in a closed whole-pond system over a 12-week period.¹³⁴ The target concentration for the application was 2.5 mg a.e./L. The half-life of triclopyr in water ranged from 5.9–7.5 days, the TCP half-life was 4–8.8 days, and TMP was 4–10 days. The sediment half-life of triclopyr was shorter, at 2.8–4.6 days; for TCP, the sediment half-life was 3.8–13.3 days. TMP was not detected in the sediment. Concentrations of triclopyr and TCP in fish matched those in the water column, but TMP concentrations were typically an order of magnitude higher, particularly in the

visceral portion of the animals. No adverse effects were observed on the non-target biotic community.

4.4.4 Garlon 4 Ultra Product Profile

The Garlon 4 Ultra product has been selected as one of the herbicides to be considered by MMWD for possible use in its Vegetation Management Plan (VMP). Garlon 4 Ultra (US EPA reg # 62719-527) contains the butoxyethyl ester (BEE) salt of triclopyr as the active ingredient (a.i.) at 43.6% weight percent, with the remaining 56.4% percent containing unspecified inert ingredients.¹⁶¹ The product contains 6.28 kg/L (5.58 lbs/gal) of the a.i., which is equivalent to 4.5 kg/L (4 lbs/gal) of the acid equivalent (a.e.) of triclopyr.¹⁶² When applied as a foliar spray, Garlon 4 Ultra is mixed at 0.5-7.5% by volume in aqueous solution with a surfactant added to aid penetration of the a.i. through the waxy cuticle of the plant surface. The maximum label application rate to brush and forests is 1.5 gallons of product per acre per year and 6.75 kg/ha, and 9 kg/ha for perennial weeds. Probable application rates that may be used by MMWD are anticipated to be 1-2 lbs/acre. The label recommends use of no more than 1-2 quarts of surfactant per acre. When applied as a cut-stump treatment, Garlon 4 Ultra is used full-strength or diluted 1 part triclopyr to 3 parts water and/or surfactant.

EPA has given this product an acute hazard warning label of Caution, placing it in Category 3 (Category 4 for inhalation exposure).¹⁶³ This rating means that the product is considered to be “Slightly toxic.” Exposure to skin or eyes may cause severe skin irritation and slight eye irritation.¹⁶⁴

4.5 Exposure Assessment and Risk Characterization for Triclopyr

Assessment of risk requires knowledge of both the inherent toxicity of a chemical and the amount of exposure that is anticipated based on intended uses. Risk characterization combines the hazard and exposure data to provide a picture of risks associated with herbicide use.

This exposure analysis is divided into four categories: workers, general public, terrestrial wildlife, and aquatic life. Two types of applications are modeled: cut stump and foliar (with two types of foliar applications: backpack and ground spray). Cut-stump and basal bark applications use higher concentrations than foliar applications. Both cut-stump/basal bark and foliar application rates of triclopyr are anticipated to be the same: 1.0, 2.0, and 3.0 pounds a.e. per acre for Lower, Central and Upper exposure estimates. More information about the types of exposure scenarios considered in this risk assessment is available in Section 2.4. Toxicity reference values for triclopyr used in the analysis are discussed in Section 4.2 (humans) and Section 4.3 (animals and other organisms).

The worksheets created by the Syracuse Environmental Research Associates (SERA) for the USFS were used to calculate estimated triclopyr exposures for workers, the general public, and terrestrial and aquatic wildlife.¹⁶⁵ The details of how the exposure calculations were done are discussed in Section 2.4. Several additional exposure scenarios were added that were not in the SERA/USFS worksheets, including drinking water exposure for birds and large mammals, food consumption for a large carnivore, and a TRV comparison for tadpoles. For water contamination, scenarios for accidental spills of concentrated and diluted triclopyr products, peak runoff and

long-term runoff were evaluated to estimate herbicide concentrations in a small, thermally stratified pond and Bon Tempe Reservoir.

Finally, an additional worksheet was developed to sum the dermal and food exposures for wildlife to estimate aggregate doses. Aggregate worker exposures from multiple exposure events were also calculated. No aggregate exposures were estimated for the general public because of the low probability of multiple exposures.

Exposure scenarios were categorized qualitatively as “**Highly Probable**,” “**Probable**,” “**Possible**,” “**Improbable**” and “**Highly Improbable**.” These five categories are used throughout the exposure estimates to designate the likelihood of each scenario occurring. Common scenarios and their probabilities are summarized in Tables 2-8 through 2-11 starting on page 2-28. Assigned probabilities are based on the assumption that the application guidelines are followed.

For all of the different exposure scenarios, **Lower**, **Central** and **Upper** estimates were calculated. Upper exposure estimates are calculated by changing all parameters to values that increase estimates; Lower estimates are obtained by changing all parameters to values that decrease estimates; and Central estimates use parameter values that are perceived as most realistic. See Section 2.4 for a complete description of parameter values used in the calculations.

Exposure estimates for humans and wildlife are presented and compared to human reference doses (RfDs) and wildlife toxicity reference values (TRVs) to give hazard quotients (HQs) that provide an estimate of risk from different exposure scenarios. Hazard quotients above one indicate that exposure exceeds the level of concern, and humans or wildlife may be at risk of adverse effects. These scenarios are flagged as potentially problematic and recommendations are made for avoiding them. Hazard quotients between 0.1 and 1.0 suggest that there may be particularly sensitive individuals or species that may be affected. Hazard quotients below 0.1 indicate low levels of risk for the effects that have been studied and are represented by the TRVs. In this document, hazard quotients less than one are reported as a percent of the TRV; HQs greater than one are reported as a multiplier of the TRV, e.g. “the HQ was 2.4 times the TRV.”

No assessment of risks could be performed for the unidentified “inert” ingredients in Garlon 4 Ultra—56% of the product by weight, some of which is a methylated seed oil of low toxicity, but not all ingredients are identified. The same is true of the inert ingredients in Garlon 3A—55.6% of the product weight is a combination of ethanol, triethylamine, and ethylenediaminetetraacetic acid. Both Garlon 4 Ultra and Garlon 3A are usually mixed with a surfactant prior to use. The toxicity of mixtures of triclopyr BEE or triclopyr TEA with each of the surfactants being considered for use by MMWD—Competitor and Sylgard 309—is not fully known. See Chapter 8 for more discussion of surfactants.

4.5.1 Chemical-Specific Exposure Parameters

Many of the parameters used to estimate exposure are constant from chemical to chemical, e.g., typical amounts of food consumed, surface area of a child, and body weight, among others. These parameters and the values used in the exposure models are discussed in Section 2.4. Other parameters, such as dermal absorption coefficients and water contamination rates, are chemical-

specific and are based on experimental data and/or physical properties such as water solubility, K_{ow} , vapor pressure, K_{oc} and half-life.

Table 4-12 presents the triclopyr-specific parameters used in the calculations, including dermal absorption rates, bioconcentration factors, half-lives, and triclopyr runoff rates. Dermal absorption rates differ between triclopyr BEE and TEA, but bioconcentration factors, half-lives, and triclopyr runoff rates are the same for the two chemicals. In general, long-term exposures are the same for triclopyr BEE and TEA because both chemicals break-down to form triclopyr acid and TCP. Short-term exposures may differ due to higher dermal permeability and higher aquatic toxicity of triclopyr BEE.

As discussed in Section 2.4.3A, USFS/SERA developed an estimate of dermal absorption rates based on K_{ow} and molecular weight.¹⁶⁶ For triclopyr BEE, first-order absorption rates were obtained in biomonitoring studies using human volunteers.¹⁶⁷ The empirical absorption rate was found to be 0.041 hour⁻¹ with a 95% confidence interval of 0.00027 and 0.068 hour⁻¹.

Empirically measured rates were used in triclopyr BEE exposure estimates. Comparing empirical triclopyr BEE first-order dermal absorption to estimated dermal absorption rates, shows that estimated rates are 16 times less than the empirically measured rates. Since there were no dermal absorption rates for triclopyr TEA, the estimated first order rates were multiplied by 16. For both triclopyr BEE and triclopyr TEA the zero-order dermal permeability rates (in units of cm/hr) come from the estimated absorption rates because no empirical rates were found.

For the rest of the triclopyr-specific chemical parameters, the same values are used for triclopyr TEA and BEE. General worker exposure rates (in mg/kg per lb/acre applied) are derived from biomonitoring studies in workers.^{168a-c} Urine concentrations of triclopyr following general exposure were varied from 0.0003 to 0.014 mg/kg per lb a.i. handled (average 0.004 mg/kg per lb a.i.). The bioconcentration factor used by the USFS is derived from experimental data showing BCFs of 0.06 when only fish flesh was eaten (human scenarios) and 0.83 when the whole fish was eaten (wildlife scenarios).¹⁶⁹ Triclopyr runoff rates are discussed in more detail in Section 4.5.3 on Water Contamination Estimates below.

Table 4-12: Triclopyr-Specific Exposure Parameters

Parameter	Lower Value	Central Value	Upper Value
Triclopyr BEE and Triclopyr TEA			
Water contamination rate, acute (mg/L per lb/acre)	0.001	0.09	0.4
Water contamination rate, chronic (mg/L per lb/acre)	0.008	0.03	0.05
Bioconcentration for fish flesh (L/kg fish)	0.06	0.06	0.06
Bioconcentration for whole fish (L/kg fish)	0.83	0.83	0.83
Half-life as residue in soil and on food (days)	26	38	69
Triclopyr BEE			
First-order dermal absorption rate (h ⁻¹)	0.00027	0.041	0.068
Dermal permeability (cm/hr)	0.0044	0.0082	0.015
Triclopyr TEA			
First-order dermal absorption rate (h ⁻¹)	0.0049	0.014	0.041
Dermal permeability (cm/hr)	0.000011	0.000024	0.000054

Data source: Reference 165. USFS worksheet B0.

Brenton VMS listed the following techniques as potential strategies for controlling invasive species with triclopyr on MMWD lands:

- High volume foliar applications to control broom at 1 pound per acre
- Low volume foliar applications to control broom at 1-2 pounds per acre
- Spot foliar applications to control thistle at 0.5 pounds per acre
- Cut stump and basal bark applications at 1-2 pounds per acre

The application rates and volumes listed in Table 4-13 were used to calculate Lower, Central and Upper exposure estimates for workers, the general public, and terrestrial and aquatic wildlife. Brenton VMS also specified the percent volume of each chemical being used. Since Garlon 3A (the product containing triclopyr TEA) has a lower concentration of active ingredient (3 lb/gallon) than Garlon 4 Ultra (triclopyr BEE at 4 lb/gallon), the volumes of the field solution had to be adjusted.

The triclopyr BEE foliar scenarios are designed to encompass both low-volume (10-25 gallons per acre) and high-volume (25-50 gallons per acre) applications. For triclopyr TEA these volumes were increased slightly to 13-33 and 33-67 for low and high volume applications respectively. The lowest concentration of chemical used is 0.5% Garlon 4 Ultra or Garlon 3A by volume (i.e. 1 quart, which is also 1 pound acid equivalent, of Garlon 4 Ultra in 200 quarts of surfactant and water mixture or 1.33 quarts of Garlon 3A in 66 gallons). The highest concentration anticipated is 7.5% for Garlon 4 Ultra and Garlon 3A by volume. The cut-stump or basal bark application scenario assumes that Garlon 4 Ultra or Garlon 3A is diluted with surfactant until it is 25% and 33% by volume, respectively. We designate solutions designed for cut-stump/basal bark applications “concentrated” and solutions for foliar application “diluted.”

Note that the application rates for foliar and cut-stump treatments are the same, thus many of the exposure estimates will be identical for the two types of applications. Accidental spill scenarios will still differ between cut-stump and foliar treatments. Also note that the concentrations used in the cut-stump method can vary. Some treatments use undiluted 100% Garlon 4 Ultra or Garlon 3A while other treatments use 25% Garlon 4 Ultra or 33% Garlon 3A by volume. These differences in concentrations are in contrast to glyphosate, where all cut-stump spill scenarios were the same due to the identical product concentrations, and results in different Upper and Central exposure estimates for triclopyr for scenarios involving a spill of cut-stump concentrations of triclopyr to water.

Table 4-13: Application Rate and Application Volume Model Inputs

Scenario		Lower	Central	Upper
Triclopyr BEE				
Foliar application	Application rate (lb a.e./acre)	1	2	3
	Percent product (volume %)	0.5	2	7.5
	Application volume (gallons)	50	25	10
Cut-stump treatments	Application rate (lb a.e./acre)	1	2	3
	Percent product (volume %)	25	25	100
	Application volume (gallons)	1	2	0.75
Triclopyr TEA				
Foliar application	Application rate (lb a.e./acre)	1	2	3
	Percent product (volume %)	0.5	2	7.5
	Application volume (gallons)	66.7	33.3	13.3
Cut-stump treatments	Application rate (lb a.e./acre)	1	2	3
	Percent product (volume %)	33	33	100
	Application volume (gallons)	1	2	1

Data source: Reference 165.

4.5.2 Application Methods for Triclopyr

Application methods that Brenton VMS recommended for use on MMWD lands for triclopyr include directed foliar, cut-stump, or basal bark (thin-line) methods. In directed foliar applications, the herbicide is applied to the target vegetation using a backpack sprayer. Chemical contact with the arms, hands, or face is Highly Improbable because of the low height of the vegetation treated. In the rare cases where vegetation exceeds a height of 100 cm, one of two additional mitigations is possible: mowing the vegetation before treatment and application methods that target the base or trunk of the plant (e.g. basal bark). To reduce the likelihood of significant exposure, application crews should not walk through treated vegetation. Usually, a worker treats approximately 0.625 acre/hour with a plausible range of 0.25–1.0 acre/hour. The number of acres treated per hour or the number of hours worked per day will likely vary amongst different MMWD application sites. Variation in these numbers will change worker exposure estimates.

The cut-stump application involves cutting the stem, and then spraying or painting Garlon 4 Ultra or Garlon 3A at a relatively high concentration (50-100% of the pure product) on the cut stump surface. Basal bark or thin-line application may also be used. Basal bark or thin-line involves applying a thin band of herbicide to the lower trunk of a target plant. Basal bark applications are less precise and use more dilute product than cut-stump applications but are more precise and concentrated than foliar applications.

4.5.3 Water Contamination Estimates

Concentration estimates for six different water contamination scenarios were calculated for triclopyr, each with Central, Lower and Upper values: four accidental spill scenarios, a peak runoff scenario and a long-term runoff scenario. Only the long-term runoff is considered Probable if the applications guidelines are adhered to. The four spill scenarios included two spill volumes (one and 20 gallons) each for a spill of the diluted product (used for foliar applications) and the concentrated product (used for cut-stump applications) to a thermally-stratified small

pond and Bon Tempe reservoir. See Section 2.4.2 for a detailed discussion of these scenarios. Results are shown in Table 4-14 for accidental spills of triclopyr BEE and TEA separately and Table 4-15 for runoff rates of triclopyr BEE and TEA together.

Table 4-14: Triclopyr BEE and TEA Concentrations for Accidental Spill Water Contamination Scenarios

Scenario		Concentration (mg/L)		
		Central	Lower	Upper
Thermally-stratified pond, triclopyr BEE				
Accidental spill of diluted product	1 gal	0.15	0.036	0.55
	20 gal	2.9	0.73	11
Accidental spill of concentrated product	1 gal	1.8	^a	7.3
	20 gal	36	^a	145
Thermally-stratified pond, triclopyr TEA				
Accidental spill of diluted product	1 gal	0.11	0.028	0.41
	20 gal	2.2	0.54	8.2
Accidental spill of concentrated product	1 gal	1.8	^a	5.5
	20 gal	36	^a	110
Well-mixed reservoir, triclopyr BEE				
Accidental spill of diluted product	1 gal	7.4x10 ⁻⁶	1.8x10 ⁻⁶	0.000028
	20 gal	0.00015	0.000037	0.00055
Accidental spill of concentrated product	1 gal	0.000092	^a	0.00037
	20 gal	0.0018	^a	0.0074
Well-mixed reservoir, triclopyr TEA				
Accidental spill of diluted product	1 gal	5.5x10 ⁻⁶	1.4x10 ⁻⁶	0.000021
	20 gal	0.00011	0.000028	0.00041
Accidental spill of concentrated product	1 gal	0.000092	^a	0.00028
	20 gal	0.0018	^a	0.0055

^a Only two estimates of concentration were calculated for spills of concentrated Garlon 4 Ultra product, 25% and 100% of Garlon 4 Ultra by volume.

Table 4-15: Triclopyr BEE and TEA Concentrations for Long-Term Runoff Water Contamination Scenarios

Scenario		Concentration (mg/L)		
		Central	Lower	Upper
Rainfall runoff, triclopyr BEE and TEA				
Peak runoff		0.18	0.0010	1.2
Long-term runoff		0.020	0.00031	0.11

Throughout this document, the word “contaminated” is used to mean that any amount of a chemical residue is present. “Contaminated” does not necessarily equate to hazardous, but indicates only that the compound is present at some level.

Predicted triclopyr water contamination rates were derived by USFS from several empirical monitoring studies.^{170a-e} Peak concentrations in stream water (excluding accidental direct spray), normalized to application rate, range from 0.033 to 0.11 mg/L per lb a.e./acre. Empirical water contamination rates match GLEAMS modeling which predicts 0.054-0.24 mg/L in a million liter pond after 50-100 inches of rain per year.

Because the USFS model does not account for seasonally strategic vegetation management that avoids the most runoff-prone conditions, the calculations for long-term runoff scenarios were adjusted for MMWD local conditions. Starting with the USFS water contamination rates, the chemical half-life (see 4-11) was used to calculate a fraction of the chemical degraded for the for 30-120 day window before the rainy season begins. This method is probably still an overestimate of water contamination rates because soils must be saturated before runoff can occur. Saturation typically occurs in November or December in Northern California, which would provide an additional 30–90 days for the chemical to degrade. See Section 2.4.2 for a detailed discussion of these and other limitations of methods used to estimate water contamination rates used in the USFS/SERA worksheets.

The only Probable water contamination scenario is the long-term runoff scenario. Peak runoff is Highly Improbable because applications would be conducted only in the dry season. Large volume accidental spills are also considered Highly Improbable.

A final calculation, described in detail in Section 2.4.2, was performed to determine the maximum volume of Garlon 4 Ultra or Garlon 3A that could be used in the MMWD watershed without exceeding triclopyr concentrations that produce an HQ > 0.1, 0.5 and 1.0 for a child drinking water from the reservoir, assuming 5% and 100% runoff of applied herbicide. Calculations were performed for both Phoenix Lake (well-mixed and thermally stratified) and Bon Tempe Reservoir to provide a range of estimates for the most broom-infested areas on MMWD lands. The results of these calculations for Phoenix Lake are presented in Table 4-16.

In the Phoenix Lake watershed, only 26 of the 214 acres of broom (excluding broom in the buffer zone¹⁷¹) could be treated with Garlon 4 Ultra and Garlon 3A without exceeding an HQ of 0.1 for the 100% runoff scenario to a well-mixed Phoenix Lake (since runoff occurs in the winter and the lake is no longer thermally stratified then). The number of acres treated is the same between Garlon 4 Ultra and Garlon 3A because it is assumed that the application rate is 2 lb/acre. The maximum volume differs because the two products have different concentrations of triclopyr (4 lb/gallon versus 3 lb/gallon). If degradation is accounted for, 80 acres could be treated. If it is determined that higher HQs are acceptable, more acres could be treated (see Table 4-16). An alternative to limiting the acres treated would be to reduce the application rate of the herbicide, as long as efficacy is maintained.

The only scenario in which all broom in the watershed outside of the buffer zone could be treated assumes a well-mixed reservoir, runoff of only 5% of the applied herbicide, and degradation of the herbicide for several months. In the Phoenix Lake watershed, restrictions on the volume of Garlon 4 Ultra that can be used in the watershed would be needed for all of the thermally-stratified scenarios to ensure that HQs not exceed 0.1 for water consumption.

Results for Bon Tempe Reservoir are not presented, but because there is slightly less broom in the Bon Tempe watershed than the Phoenix Lake watershed and the volume of the reservoir is larger than Phoenix Lake, the entire 149 acres of broom could be treated with Garlon 4 Ultra without exceeding an HQ of 0.1 for even the worst-case scenario.

Table 4-16: Maximum Volume of Garlon 4 Ultra that Could Be Applied in Phoenix Lake Watershed without Exceeding Hazard Quotients of 0.1, 0.5, and 1.0

Scenario	Volume of Garlon 4 Ultra (gal)		Volume of Garlon 3A (gal)		Maximum Area Treated at 2 lb/acre (acres)	
	Well-Mixed	Strat-ified	Well-Mixed	Strat-ified	Well-Mixed	Strat-ified
HQ = 0.1						
100% runoff, no degradation	13	0.40	18	0.53	26	0.8
100% runoff, degradation for 60 days ($t_{1/2} = 38$ days)	40	1.2	53	1.6	80	2.4
5% runoff, degradation for 60 days ($t_{1/2} = 38$ days)	790	24	1,100	32	1,600	48
HQ = 0.5						
100% runoff, no degradation	66	2	88	2.6	130	4
100% runoff, degradation for 60 days ($t_{1/2} = 38$ days)	200	6	260	7.8	400	12
5% runoff, degradation for 60 days ($t_{1/2} = 38$ days)	4,000	120	5,300	160	7,900	240
HQ = 1						
100% runoff, no degradation	130	4	180	5.2	260	8
100% runoff, degradation for 60 days ($t_{1/2} = 38$ days)	400	12	530	16	800	24
5% runoff, degradation for 60 days ($t_{1/2} = 38$ days)	7,900	240	11,000	312	16,000	480

$t_{1/2}$ = half-life of triclopyr acid

The use of 100% as the percentage of applied herbicide that runs off after an application is an overestimate. Runoff rates calculated for triclopyr by the USFS/SERA worksheets are typically much lower, ranging from less than one to 12 percent for average rainfall in Marin County. Table 4-17 and 4-18 shows estimated triclopyr BEE and TEA loss through runoff as a fraction of the application rate for various soil types. Since site-specific parameters are needed for such modeling, Table 4-17 and 4-18 serves as only a rough estimate of runoff rates for MMWD lands. The USFS/SERA worksheets (and hence the water contamination rates for the exposure estimates) do not incorporate site-specific characteristics like distance between the treatment site and the water body, volume of the water body receiving runoff, seasonality of rain, and acres treated.

Table 4-17: Fraction of Triclopyr BEE Lost as a Function of Annual Rainfall

Annual Rainfall (inches)	Fraction of Herbicide Lost on Soil Type		
	Clay	Loam	Sand
5	0	0	0
10	0	0.00047	0.0024
15	0.00091	0.0018	0.0071
20	0.0020	0.0038	0.013
25	0.0037	0.0062	0.020
50	0.013	0.020	0.056

Data source: USFS Worksheet G04.

Table 4-18: Fraction of Triclopyr TEA Lost as a Function of Annual Rainfall

Annual Rainfall (inches)	Fraction of Herbicide Lost on Soil Type		
	Clay	Loam	Sand
5	0	0	0
10	3.12x10 ⁻⁸	0.0058	0.0075
15	0.016	0.018	0.016
20	0.032	0.031	0.024
25	0.048	0.043	0.030
50	0.12	0.092	0.053

Data source: USFS Worksheet G04.

4.5.4 Risks to Humans

Exposure estimates were performed for both workers and members of the general public. Accidental/incidental and general handling exposures were considered for herbicide applicators for ground spray, backpack spraying and cut-stump applications. Public exposure estimates were developed for the scenarios of people contacting contaminated vegetation on or near an application site, eating contaminated fruit or fish, or drinking contaminated water. Acute and chronic exposure scenarios were evaluated to obtain a range of exposure estimates for both worst-case and more probable scenarios.

4.5.4.A Workers

Risks from accidental and general exposure scenarios were calculated for workers. Accidental exposures included wearing contaminated gloves for one minute and one hour, direct spray onto hands, and direct spray to lower legs. Exposure estimates from these scenarios were different for triclopyr BEE and TEA because of the two chemicals' differing dermal permeability. General exposures for backpack spraying and ground spraying were the same for triclopyr BEE and TEA.

Dermal exposure is of particular concern for triclopyr, and special application guidelines were added for triclopyr applications. Triclopyr BEE has higher dermal permeability. Workers were most at risk from wearing gloves for an hour contaminated with triclopyr BEE. The Central exposure estimate exceeding the RfD by a factor of 12 for concentrated triclopyr BEE used in cut-stump applications. Wearing contaminated gloves was much less of a hazard for triclopyr TEA, with a Central exposure estimate of 3.5% of the TRV. Spills were also problematic, with Central exposure estimates exceeding the RfD by a factor 1.1 for a spill of triclopyr BEE to the lower legs. The same scenario estimates an exposure that is 40% of the RfD for triclopyr TEA. Exposures from general handling of triclopyr BEE and TEA from backpack or ground spraying were 53% and 90% of the RfD, respectively for Central estimates and up to 4.8 and 9.1 times the RfD for Upper estimates. Doses and hazard quotients for all worker exposure scenarios can be found in Table 4-19 for triclopyr BEE and 4-20 for triclopyr TEA.

Exposure estimates from the scenarios that are the most likely to occur for workers are highlighted below:

1. **General exposure due to backpack spraying (Highly Probable) – both triclopyr BEE and TEA.** The Central dose estimate for general backpack spraying is 53% of the RfD. The

Upper estimate is 4.8 times the RfD. The dose estimates are based on application rates which are the same for both chemicals.

2. **General exposure due to ground spraying (Highly Probable) – both triclopyr BEE and TEA.** The Central dose estimate for general ground spraying is 90% of the RfD. The Upper estimate is 9.1 times the RfD. The dose estimates are based on application rates which are the same for both chemicals.
3. **Wearing contaminated gloves for one minute (Probable).**
 - a. **Triclopyr BEE:** The Central dose estimate for wearing gloves contaminated with concentrated product (cut-stump worker) for one minute is 20% of the acute RfD. The Upper estimate is 1.4 times the acute RfD. For the diluted solution (foliar worker), the Central dose estimate for wearing contaminated gloves for one minute is 1.6% of the RfD. The Upper estimate is 11% of the RfD.
 - b. **Triclopyr TEA:** The Central dose estimate for wearing gloves contaminated with concentrated product (cut-stump worker) for one minute is 0.058% of the acute RfD. The Upper estimate is 0.39% of the acute RfD. For the diluted solution (foliar worker), the Central dose estimate for wearing contaminated gloves for one minute is 0.0035% of the RfD. The Upper estimate is 0.029% of the RfD. The estimates are different because the zero-order dermal permeability of the two chemicals is quite different.
4. **Wearing contaminated gloves without washing for one hour (Improbable).**
 - a. **Triclopyr BEE:** The Central dose estimate for wearing gloves contaminated with concentrated product for one hour is 11.8 times the RfD. The Upper estimate is 86 times the RfD.
 - b. **Triclopyr TEA:** The Central dose estimate for wearing gloves contaminated with concentrated product for one hour is 3.5% of the RfD. The Upper estimate is 23% of the RfD. The estimates are different because the zero-order dermal permeability of the two chemicals is quite different.
5. **Accidental spill to the hands that is left unwashed for one hour (Improbable).**
 - a. **Triclopyr BEE:** The Central dose estimate for a spill on workers' hands that is left unwashed for one hour is 3.7% of the RfD for the diluted product and 46% of the RfD for the concentrated product. Upper estimates for diluted and concentrated product are 23% of the RfD and 3.0 times the RfD, respectively.
 - b. **Triclopyr TEA:** The Central dose estimate for a spill on workers' hands that is left unwashed for one hour is 0.96% of the RfD for the diluted product and 16% of the RfD for the concentrated product. Upper estimates for diluted and concentrated product are 10% of the RfD and 1.4 times the RfD, respectively.
6. **Accidental spill to the lower legs that is left unwashed for one hour (Improbable).**
 - a. **Triclopyr BEE:** The Central dose estimate for a spill of diluted product to the lower legs that is left unwashed for one hour is 9.1% of the RfD. The Upper estimate is 56% of the RfD. The Central dose estimate for a spill of concentrated product to the lower legs that is left unwashed for one hour is 1.1 times the RfD. The Upper estimate is 7.5 times the RfD.
 - b. **Triclopyr TEA:** The Central dose estimate for a spill of diluted product to the lower legs that is left unwashed for one hour is 2.4% of the RfD. The Upper estimate is 26% of the RfD. The Central dose estimate for a spill of concentrated product to the lower legs that is left unwashed for one hour is 40% of the RfD. The Upper estimate is 3.4 times the RfD.

For women applicators of childbearing age, hazard quotients for acute spill exposures are 20 times those discussed above. The acute RfD for women is 0.05 mg/kg-day, not 1.0 mg/kg-day, due to the risk of birth defects. We recommend that for all workers with the potential for exposure to triclopyr and triclopyr-treated vegetation, MMWD require training regarding the specific risks associated with exposure in excess of that required by OSHA and Cal-DPR standards.

If accidental worker exposures occur, the dose from that scenario must be added to the general exposure to obtain an aggregate dose. For example, if a worker sprays vegetation with a backpack sprayer for eight hours and also wears a contaminated glove for one hour, the combined Central exposure estimate for triclopyr BEE is $0.24 + 11.8 = 12.04$ mg/kg-day. In this case, the spill exposure estimates are much higher than the general exposure for triclopyr, thus general exposure does not contribute significantly to the aggregate exposure. However, multiple spills and continued wearing of contaminated gloves would quickly add up to very high aggregate exposures and must be avoided.

A contributing factor to the high worker risks calculated for triclopyr is that it is assumed applicators may be applying triclopyr regularly over one to six months. For these short- and intermediate-term exposures, EPA uses the short-term RfD of 0.05 mg/kg, a factor of 20 lower than the acute RfD of 1.0 mg/kg. For women applicators, the RfD of 0.05 applies to all scenarios, both acute and chronic, because of risks of birth defects if the woman is pregnant.

These exposure estimates do not include splashes into the eyes, as there are no quantitative, systemic exposure estimates for this scenario. Garlon 4 Ultra is slightly irritating to the eyes,¹⁶¹ but little systemic absorption would be expected from such an event. Garlon 3A is a severe eye irritant, warranting its classification as a Category I (DANGER) product.

Confidence in these exposure assessments is reasonably high because of the availability of dermal absorption data in humans as well as worker exposure studies. All estimates assume workers wear personal protective equipment.

We conclude that the most significant risk to workers is from dermal exposure due to accidental spills. The risk is significantly greater for women of child-bearing age. Precautions should be taken to avoid spills to unprotected skin and eyes, including the use of goggles, double gloves, long-sleeved clothing and closed shoes. Applicators should have extra clean gloves readily available, soap and water for washing off spills, and an eyewash bottle in their vehicle at all times. Rubber boots are highly recommended. If triclopyr is to be used, MMWD must adequately train applicators in avoiding direct contact with the chemical.

Table 4-19: Estimated Triclopyr BEE Exposures and Hazard Quotients for Workers

Scenario	Calculated Dose (mg/kg)			RfD (mg/kg-day)	Hazard Quotient (HQ)		
	Central	Lower	Upper		Central	Lower	Upper
Foliar Worker Accidental/Incidental Exposures (dose in mg/kg-event)							
Contaminated gloves, 1 min	0.016	0.0021	0.11	1	0.016	0.0021	0.11
Contaminated gloves, 1 h	0.94	0.13	6.48	1	0.94	0.13	6.5
Spill on hands, 1 h	0.037	0.000062	0.23	1	0.037	0.000062	0.23
Spill on lower legs, 1 h	0.091	0.00015	0.56	1	0.091	0.00015	0.56
Cut Stump Worker Accidental/Incidental Exposures (dose in mg/kg-event)							
Contaminated gloves, 1 min	0.20	0.11	1.4	1	0.20	0.11	1.4
Contaminated gloves, 1 h	12	6.3	86	1	12	6.34	86
Spill on hands, 1 h	0.46	0.0031	3.0	1	0.46	0.0031	3.0
Spill on lower legs, 1 h	1.1	0.0077	7.5	1	1.1	0.0077	7.5
Foliar Worker General Exposures (mg/kg-day)							
General exposure, backpack spraying	0.026	0.00045	0.24	0.05	0.53	0.0090	4.8
General exposure, ground spraying	0.045	0.00066	0.45	0.05	0.90	0.013	9.1
Cut Stump Worker General Exposures (mg/kg-day)							
General exposure, backpack spraying	0.026	0.00045	0.24	0.05	0.53	0.0090	4.8

RfD = Reference dose. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are also **bolded**.

Table 4-20: Estimated Triclopyr TEA Exposures and Hazard Quotients for Workers

Scenario	Calculated Dose (mg/kg)			RfD (mg/kg-day)	Hazard Quotient (HQ)		
	Central	Lower	Upper		Central	Lower	Upper
Foliar Worker Accidental/Incidental Exposures (dose in mg/kg-event)							
Contaminated gloves, 1 min	0.000035	4.0x10 ⁻⁶	0.00029	1	0.000035	4.0x10 ⁻⁶	0.00029
Contaminated gloves, 1 h	0.0021	0.00024	0.018	1	0.0021	0.00024	0.018
Spill on hands, 1 h	0.0096	0.00085	0.10	1	0.0096	0.00085	0.10
Spill on lower legs, 1 h	0.024	0.0021	0.26	1	0.024	0.0021	0.26
Cut Stump Worker Accidental/Incidental Exposures (dose in mg/kg-event)							
Contaminated gloves, 1 min	0.00058	0.00026	0.0039	1	0.00058	0.00026	0.0039
Contaminated gloves, 1 h	0.035	0.016	0.23	1	0.035	0.016	0.23
Spill on hands, 1 h	0.16	0.056	1.4	1	0.16	0.056	1.4
Spill on lower legs, 1 h	0.40	0.14	3.4	1	0.40	0.14	3.4
Foliar Worker General Exposures (mg/kg-day)							
General exposure, backpack spraying	0.026	0.00045	0.24	0.05	0.53	0.0090	4.8
General exposure, ground spraying	0.045	0.00066	0.45	0.05	0.90	0.013	9.1
Cut Stump Worker General Exposures (mg/kg-day)							
General exposure, backpack spraying	0.026	0.00045	0.24	0.05	0.53	0.0090	4.8

RfD = Reference dose. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are also **bolded**.

4.5.4.B General Public

Acute and chronic triclopyr exposure scenarios for the general public were evaluated for direct spray onto a person, contact with contaminated vegetation, and consumption of contaminated fruit, fish and water. The general public is at lower risk than workers because they are less likely

to come into direct dermal contact with the chemical; however, dermal exposure remains the most hazardous exposure route for the general public. Estimated exposures are summarized for different scenarios in Table 4-21 for acute exposure to triclopyr BEE, Table 4-22 for acute exposure to triclopyr TEA and Table 4-23 for chronic exposure to either chemical. Long-term exposures are the same for triclopyr BEE and TEA because both chemicals break-down to form triclopyr acid and TCP. Short-term exposures may differ due to higher dermal permeability and slightly higher aquatic toxicity of triclopyr BEE.

The scenario with the highest exposure potential is brushing against contaminated vegetation, with Central estimates equal to 2.8 times the RfD for women and Upper estimates 5.6 times the RfD for triclopyr BEE. For triclopyr TEA the same scenario leads to exposures that exceed the RfD by 1.3 times and 4.4 times the RfD for the Central and Upper estimates respectively. If the Application Guidelines (Section 2. 5.1) are adhered to and application sites are posted, this route of exposure becomes Improbable.

Contamination of drinking water reservoirs from long-term runoff of triclopyr in the watershed is Probable, and hazard quotients begin to approach levels of concern for women, at 5% of the RfD for the Central estimate and 35% of the RfD for the Upper estimate. Taking the precaution of limiting the amount of triclopyr used in the watershed would substantially reduce the probability of exposures above levels of concern for triclopyr.

Only one exposure route is considered to be Possible for the general public:

A man consuming contaminated fish after long-term runoff (Possible). The Upper chronic dose estimates for triclopyr BEE and TEA for a man eating contaminated fish is 0.015% of the RfD. The Central estimate is substantially lower, indicating that this scenario would not be a major contributor to overall exposure. The exposure estimate is the same for triclopyr BEE and TEA because it is based on the application rate of the chemical.

It is also useful to consider the scenarios that yield the highest exposures, regardless of their probability, to evaluate the potential need for additional precautions that might be needed to protect the public. A number of Central exposure scenarios result in HQs above 1 for triclopyr:

1. **A woman drinking from a thermally stratified, small pond contaminated with a 20-gallon spill (Highly Improbable) – both triclopyr BEE and TEA.** The Central dose estimate for a woman drinking from a pond into which 20 gallons of concentrated triclopyr product spilled is 23 times the RfD. These Central values are the same for triclopyr BEE and TEA because the concentration of the concentrated solution was fixed at 1 lb/gallon.
2. **Direct spray of a child over its entire body (Highly Improbable) – both**
 - a. **Triclopyr BEE:** Direct sprays with either concentrated or diluted product resulted in high exposures, exceeding the RfD by a factor of 1.4–17 for the Central estimate.
 - b. **Triclopyr TEA:** Direct sprays with either concentrated or diluted product resulted in high exposures, either 40% of the RfD or 6 times the RfD for the Central estimate. These values are not the same for triclopyr BEE and TEA because the dermal absorption is different between the two chemicals.

3. **A woman consuming contaminated berries (Improbable) – both triclopyr BEE and TEA.** The Central chronic dose estimate for a woman eating berries contaminated by diluted or concentrated triclopyr product is 48% of the RfD for women). The Upper estimate is 11 times the RfD. These values are the same for triclopyr BEE and TEA because the exposure estimate is based on the application rate.
4. **A woman brushing against vegetation contaminated with diluted or concentrated product (Improbable).**
 - a. **Triclopyr BEE:** The Central dose estimate for a woman brushing against contaminated vegetation for either of these scenarios is 2.8 times the RfD. The Upper estimate is 5.6 times the RfD. These values are the same for triclopyr BEE and TEA because the exposure estimate is based on the application rate.
 - b. **Triclopyr TEA:** The Central dose estimate for a woman brushing against contaminated vegetation for either of these scenarios is 1.3 times the RfD. The Upper estimate is 4.4 times the RfD. These values are not the same for triclopyr BEE and TEA because the dermal absorption is different between the two chemicals.

The scenario of brushing against contaminated vegetation could lead to exposures above the RfD. The likelihood of exposures from this route can be reduced to Improbable by trimming or mowing vegetation prior to treatment and posting the treated area.

The scenario of eating contaminated berries is Improbable if the application guidelines are followed. In order to reduce the probability of exposures, the public should be made aware of application timing and locations, and berry bushes or other edible plants should be trimmed or mowed before herbicide treatments. Conducting applications during the week instead of on the weekend, limiting access to application sites, and avoiding off-target direct sprays to blackberry, blueberry (huckleberry), thimbleberry, hazelnut, and manzanita plants will help ensure public safety.

If triclopyr is to be used, MMWD should take precautions to prevent the public from accessing application sites. Such precautions might include: prohibiting applications to vegetation within five feet of a trail; applying only to the upslope or non-trail-facing side of vegetation; fencing or signing treated vegetation to prevent accidental contact; temporarily tarping the treated portion of vegetation to prevent accidental dermal contact; and temporarily closing trails.

Water Consumption Scenarios: Only the Highly Improbable scenario in which a woman or child drinks from a thermally stratified pond contaminated with diluted or concentrated product resulted in Central HQs greater than 1.0. A 20-gallon spill of concentrated Garlon 3A or Garlon 4 Ultra resulted in an HQ=23 times the RfD for a woman.

Concentrations of triclopyr from spills into a reservoir like Bon Tempe were lower than those for spills into a small pond by a factor of nearly 20,000, and HQs are substantially less than one. A spill of 20 gallons of either concentrated Garlon 4 Ultra or concentrated Garlon 3A, results in an HQ of 0.12% of the RfD for the Central exposure estimate for an adult woman drinking out of Bon Tempe reservoir. Adherence to the MMWD application guidelines would make a high-volume spill of concentrated product into a reservoir Highly Improbable, and with a plan in place to notify water treatment plants if such a spill were to occur, we conclude that it is Highly

Improbable that drinking water quality in MMWD reservoirs will be compromised by spills of triclopyr into the reservoirs.

Contamination by long-term runoff is Probable if many acres are treated in a single year. The Central estimated concentrations is 5.2% of the RfD for a woman. The Upper estimate is 35% of the RfD. These values are the same for triclopyr BEE and triclopyr TEA. This calculation provides an estimate of water contamination based on application rate and may *underestimate* concentrations if more than 10 acres are treated. The calculation may *overestimate* concentrations for runoff into water bodies larger than a small pond (i.e., all of the the MMWD reservoirs are much larger than the small pond used in the calculation), and for applications in which a buffer zone is used. See Section 4.5.3 and Section 2.5.2 for a more detailed discussion.

As a check on the USFS worksheet number, calculations were performed to estimate concentrations for a worst-case scenario (Section 4.5.3), assuming that all 214 acres of broom in the Phoenix Lake watershed were treated with Garlon 4 Ultra or Garlon 3A at 2.0 lbs/acre. If 100% of the applied herbicide ran off into Phoenix Lake during the winter rainy season, the HQ for a child drinking water from the reservoir would be 73% of the RfD. This is a worst-case scenario that is unlikely to occur, since 100% of the herbicide will not run off (1–6% is a more realistic estimate for triclopyr BEE and 6-12% for triclopyr TEA, see Tables 4-17 and 4-18). Further, Phoenix Lake is not currently used as part of Marin's a water supply. The larger Bon Tempe reservoir would dilute any runoff by a factor of 9.75 compared to Phoenix Lake, and there is considerably less broom in the Bon Tempe watershed. Adjusting the parameters to a more realistic, but still high-end scenario (6% runoff into Bon Tempe Reservoir, 214 acres treated) gives an HQ of 0.5% of the RfD. Treatment of fewer acres each year and use of buffer zones around water bodies (as the MMWD application guidelines require) would reduce HQs further.

Table 4-21: Estimated Acute Triclopyr BEE Exposures and Hazard Quotients for the General Public

Scenario	Receptor	Calculated Dose (mg/kg-event)			RfD (mg/kg-day)	Hazard Quotient (HQ)		
		Central	Lower	Upper		Central	Lower	Upper
Acute exposure estimates for diluted triclopyr product (foliar treatment)								
Direct spray of child, whole body	Child	1.40	0.0024	8.58	1	1.40	0.0024	8.58
Direct spray of woman, feet, lower legs	Adult female	0.14	0.00024	0.86	0.05	2.80	0.0048	17.2
Vegetation contact, shorts and T-shirt	Adult female	0.14	0.00068	0.28	0.05	2.80	0.014	5.6
Contaminated fruit consumption	Adult female	0.024	0.0034	0.56	0.05	0.48	0.068	11.2
Water consumption (pond) after	Adult female	0.0046	0.00079	0.020	0.05	0.091	0.016	0.41
	1 gal spill							
	20 gal spill					1.83	0.31	8.12
Water consumption (reservoir) after	Adult female	2.3x10 ⁻⁷	4.0x10 ⁻⁸	1.0x10 ⁻⁶	0.05	4.57x10 ⁻⁶	8.01x10 ⁻⁷	0.000021
	1 gal spill							
	20 gal spill					0.000091	0.000016	0.00041
Water consumption after peak runoff	Adult female	0.0056	0.000022	0.045	0.05	0.12	0.000044	0.93
Fish consumption (pond) after	Adult male	9.5x10 ⁻⁶	2.4x10 ⁻⁶	0.000036	1	9.5x10 ⁻⁶	2.4x10 ⁻⁶	0.000036
	1 gal spill							
	20 gal spill					0.00019	0.000047	0.00071
Fish consumption (reservoir) after	Adult male	4.8 x10 ⁻¹⁰	1.2 x10 ⁻¹⁰	1.8x10 ⁻⁹	1	4.8 x10 ⁻¹⁰	1.2 x10 ⁻¹⁰	1.8x10 ⁻⁹
	1 gal spill							
	20 gal spill					9.6 x10 ⁻⁹	2.4 x10 ⁻⁹	3.6 x10 ⁻⁸
Fish consumption (pond) after	Subsistence male	0.000096	0.000024	0.00036	1	0.000096	0.000024	0.00036
	1 gal spill							
	20 gal spill					0.0019	0.00048	0.0072
Fish consumption (reservoir) after	Subsistence male	4.9x10 ⁻⁹	1.2x10 ⁻⁹	1.8x10 ⁻⁸	1	4.9x10 ⁻⁹	1.2x10 ⁻⁹	1.8x10 ⁻⁸
	1 gal spill							
	20 gal spill					9.7x10 ⁻⁸	2.4 x10 ⁻⁸	3.7x10 ⁻⁷
Acute exposure estimates for concentrated triclopyr product (cut-stump treatment)								
Direct spray of child, whole body	Child	17	0.12	114	1	17	0.12	110
Direct spray of woman, feet, lower legs	Adult female	1.76	0.012	11.5	0.05	35	0.24	230
Vegetation contact, woman in shorts and T-shirt	Adult female	0.14	0.00068	0.28	0.05	2.81	0.014	5.6
Contaminated fruit consumption	Adult female	0.024	0.0034	0.56	0.05	0.47	0.068	11
Water consumption (pond) after	Adult female	0.057	0.040	0.27	0.05	1.1	0.80	5.3
	1 gal spill							
	20 gal spill					23	16	110
Water consumption (reservoir) after	Adult female	2.9x10 ⁻⁶	2.0 x10 ⁻⁶	0.000014	0.05	0.000057	0.000040	0.00027
	1 gal spill							
	20 gal spill					0.000056	0.000040	0.00028
Water consumption after peak runoff	Adult female	0.0056	0.000022	0.045	0.05	0.11	0.000044	0.93
Fish consumption (pond) after	Adult male	0.00012	^c	0.00047	1	0.00012	^c	0.00047
	1 gal spill							
	20 gal spill					0.0024	^c	0.0096
Fish consumption (reservoir) after	Adult male	6.0x10 ⁻⁹	^c	2.4x10 ⁻⁸	1	6.0x10 ⁻⁹	^c	2.4x10 ⁻⁸
	1 gal spill							
	20 gal spill					1.2x10 ⁻⁷	^c	4.8x10 ⁻⁷
Fish consumption (pond) after	Subsistence male	0.0012	^c	0.0048	1	0.0012	^c	0.0048
	1 gal spill							
	20 gal spill					0.024	^c	0.096
Fish consumption (reservoir) after	Subsistence male	6.1x10 ⁻⁸	^c	2.4x10 ⁻⁷	1	6.1x10 ⁻⁸	^c	2.4x10 ⁻⁷
	1 gal spill							
	20 gal spill					1.2x10 ⁻⁶	^c	4.8 x10 ⁻⁶

RfD = Reference Dose. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are also bolded.

^aThe anticipated application rate for cut-stump and foliar applications is the same, resulting in identical exposure estimates for the two scenarios.

^bIn the long-term runoff scenario, we assume that a large fraction of triclopyr has degraded to form TCP, which has a lower RfD than triclopyr BEE

^cOnly two estimates of concentration were calculated for spills of concentrated Garlon 4 Ultra product, 25% and 100% of Garlon 4 Ultra by volume.

^dLong-term runoff was estimated using the USFS worksheets based on application rate [(mg/L)/(lb/acre)] and is not specific to a particular water body. See Section 2.4.2 for more discussion of this topic.

Table 4-22: Estimated Acute Triclopyr TEA Exposures and Hazard Quotients for the General Public

Scenario	Receptor	Calculated Dose (mg/kg-event)			RfD (mg/kg-day)	Hazard Quotient (HQ)		
		Central	Lower	Upper		Central	Lower	Upper
Acute exposure estimates for diluted triclopyr TEA product (foliar treatment)								
Direct spray of child, whole body	Child	0.36	0.032	3.9	1	0.36	0.032	4
Direct spray of woman, feet, lower legs	Adult female	0.036	0.0032	0.40	0.05	0.74	0.064	8
Vegetation contact, shorts and T-shirt	Adult female	0.064	0.012	0.22	0.05	1.3	0.24	4.4
Contaminated fruit consumption	Adult female	0.024	0.0034	0.56	0.05	0.48	0.068	11.2
Water consumption (pond) after 1 gal spill	Adult female	0.0034	0.00060	0.015	0.05	0.068	0.012	0.30
20 gal spill	Adult female	0.068	0.012	0.31	0.05	1.4	0.24	6.2
Water consumption (reservoir) after 1 gal spill	Adult female	1.7x10 ⁻⁷	3.0x10 ⁻⁸	7.8x10 ⁻⁷	0.05	3.4x10 ⁻⁶	6.0x10 ⁻⁷	0.000015
20 gal spill	Adult female	3.5x10 ⁻⁶	6.0x10 ⁻⁷	0.000016	0.05	0.000070	0.000012	0.00032
Water consumption after peak runoff	Adult female	0.0056	0.000022	0.045	0.05	0.11	0.00044	0.90
Fish consumption (pond) after 1 gal spill	Adult male	7.1x10 ⁻⁶	1.8x10 ⁻⁶	0.000027	1	7.1x10 ⁻⁶	1.8x10 ⁻⁶	0.000027
20 gal spill	Adult male	0.00014	0.000036	0.00053	1	0.00014	0.000035	0.00053
Fish consumption (reservoir) after 1 gal spill	Adult male	3.6 x10 ⁻¹⁰	9.0 x10 ⁻¹¹	1.3x10 ⁻⁹	1	3.6 x10 ⁻¹⁰	9.0 x10 ⁻¹¹	1.4x10 ⁻⁹
20 gal spill	Adult male	7.2 x10 ⁻⁹	1.8 x10 ⁻⁹	2.7 x10 ⁻⁸	1	7.2 x10 ⁻⁹	1.8 x10 ⁻⁹	2.7 x10 ⁻⁸
Fish consumption (pond) after 1 gal spill	Subsistence male	0.000072	0.000018	0.00027	1	0.000072	0.000018	0.00027
20 gal spill	Subsistence male	0.0014	0.00036	0.0054	1	0.0014	0.00036	0.0054
Fish consumption (reservoir) after 1 gal spill	Subsistence male	3.6x10 ⁻⁹	9.1x10 ⁻¹⁰	1.4x10 ⁻⁸	1	3.7x10 ⁻⁹	9.1x10 ⁻¹⁰	1.4x10 ⁻⁸
20 gal spill	Subsistence male	7.3x10 ⁻⁸	1.8 x10 ⁻⁸	2.7x10 ⁻⁷	1	7.3x10 ⁻⁸	1.8 x10 ⁻⁸	2.7x10 ⁻⁷
Acute exposure estimates for concentrated triclopyr TEA product (cut-stump treatment)								
Direct spray of child, whole body	Child	6.1	2.1	53	1	6.1	2.1	53
Direct spray of woman, feet, lower legs	Adult female	0.61	0.21	5.3	0.05	12	4.2	106
Vegetation contact, shorts and T-shirt	Adult female	0.064	0.012	0.22	0.05	1.3	0.24	4.4
Contaminated fruit consumption	Adult female	0.024	0.0034	0.56	0.05	0.48	0.068	11.2
Water consumption (pond) after 1 gal spill ^c	Adult female	0.057	0.040	0.20	0.05	1.1	0.80	4
20 gal spill	Adult female	1.1	0.79	4.1	0.05	23	16	82
Water consumption (reservoir) after 1 gal spill	Adult female	2.9x10 ⁻⁶	2.0 x10 ⁻⁶	0.000010	0.05	0.000058	0.000040	0.00020
20 gal spill	Adult female	0.000058	0.000040	0.00021	0.05	0.0012	0.00080	0.0042
Water consumption after peak runoff	Adult female	0.0056	0.000022	0.045	0.05	0.11	0.00044	0.90
Fish consumption (pond) after 1 gal spill	Adult male	0.00012	^c	0.00036	1	0.00012	^c	0.00036
20 gal spill	Adult male	0.0024	^c	0.0071	1	0.0024	^c	0.0071
Fish consumption (reservoir) after 1 gal spill	Adult male	6.0x10 ⁻⁹	^c	1.8x10 ⁻⁸	1	6.0x10 ⁻⁹	^c	1.8x10 ⁻⁸
20 gal spill	Adult male	1.2x10 ⁻⁷	^c	3.6x10 ⁻⁷	1	1.2x10 ⁻⁷	^c	3.6x10 ⁻⁷
Fish consumption (pond) after 1 gal spill	Subsistence male	0.0012	^c	0.0036	1	0.0012	^c	0.0036
20 gal spill	Subsistence male	0.024	^c	0.072	1	0.024	^c	0.072
Fish consumption (reservoir) after 1 gal spill	Subsistence male	6.1x10 ⁻⁸	^c	1.8x10 ⁻⁷	1	6.1x10 ⁻⁸	^c	1.8x10 ⁻⁷
20 gal spill	Subsistence male	1.2x10 ⁻⁶	^c	3.7 x10 ⁻⁶	1	1.2x10 ⁻⁶	^c	3.7 x10 ⁻⁶

RfD = Reference Dose. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are also bolded.

^aThe anticipated application rate for cut-stump and foliar applications is the same, resulting in identical exposure estimates for the two scenarios.

^bIn the long-term runoff scenario, we assume that a large fraction of triclopyr has degraded to form TCP, which has a lower RfD than triclopyr BEE

^cOnly two estimates of concentration were calculated for spills of concentrated Garlon 4 Ultra product, 25% and 100% of Garlon 4 Ultra by volume.

^dLong-term runoff was estimated using the USFS worksheets based on application rate [(mg/L)/(lb/acre)] and is not specific to a particular water body. See Section 2.4.2 for more discussion of this topic.

Table 4-23: Estimated Chronic Triclopyr BEE and TEA Exposures and Hazard Quotients for the General Public

Scenario	Receptor	Calculated Dose (mg/kg-event)			RfD (mg/kg-day)	Hazard Quotient (HQ)		
		Central	Lower	Upper		Central	Lower	Upper
Chronic exposure estimates for diluted (foliar treatment) and concentrated (cut stump) triclopyr TEA product^a								
Fruit consumption	Adult female	0.011	0.0013	0.37	0.012 ^b	0.96	0.11	31
Water consumption ^d	Adult female	0.00062	6.9x10 ⁻⁶	0.0042	0.012 ^b	0.052	0.00057	0.35
Water consumption ^d	Adult male	0.00057	6.3x10 ⁻⁶	0.0038	0.05	0.011	0.00013	0.076
Fish consumption ^d	Adult male	1.3x10 ⁻⁶	2.1x10 ⁻⁸	7.2x10 ⁻⁶	0.05	0.000026	4.1x10 ⁻⁷	0.00015
Fish consumption ^d	Subsistence male	1.4x10 ⁻⁶	2.2x10 ⁻⁸	0.000073	0.05	0.000028	4.4x10 ⁻⁷	0.0015

RfD = Reference Dose. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are also **bolded**.

^aThe anticipated application rate for cut-stump and foliar applications is the same, resulting in identical exposure estimates for the two scenarios.

^bIn the long-term runoff scenario, we assume that a large fraction of triclopyr has degraded to form TCP, which has a lower RfD than triclopyr TEA

^cOnly two estimates of concentration were calculated for spills of concentrated Garlon 3A product, 25% and 100% of Garlon 3A by volume.

^dLong-term runoff was estimated using the USFS worksheets based on application rate [(mg/L)/(lb/acre)] and is not specific to a particular water body. See Section 2.4.2 for more discussion of this topic.

4.5.5 Risks to Wildlife

The wildlife risk assessment is divided into two parts, terrestrial and aquatic. Aquatic wildlife are at much greater risk from triclopyr exposure compared to terrestrial wildlife. Several terrestrial scenarios produced HQs greater than one for a single exposure. Aggregate triclopyr doses from dermal exposure and food consumption for insectivorous and herbivorous small mammals produced hazard quotients for Central exposure estimates greater than 10% of the TRVs. The Upper estimate for one of these scenarios exceeded an HQ of 1. The only aquatic scenario considered Possible is the long-term runoff scenario. Exposures from this scenario exceeded TRVs for Upper estimates of triclopyr exposure for fish, aquatic invertebrates and aquatic plants. Central hazard quotients were all greater than 20% of the TRVs for these species.

4.5.5.A Terrestrial Wildlife

As of 1993, the MMWD had cataloged 287 vertebrate species in the watershed, 54 of which are mammals and 202 are birds. The wildlife scenarios developed in the SERA worksheets are representative of MMWD wildlife. Tables 4-24 through 4-26 show the acute, chronic and aggregate triclopyr exposure estimates and hazard quotients for terrestrial wildlife. Tables 4-24 and 4-26 include different exposure estimates and HQs for triclopyr BEE and TEA. The long-term exposures in Table 4-25 are the same for triclopyr BEE and TEA because both chemicals break-down to form triclopyr acid and TCP. See Section 2.4.5 for a discussion of the methods used to estimate wildlife exposures and Section 4.3.2 on page 4-25 for a summary of triclopyr toxicity studies on terrestrial organisms and a discussion of the choice of specific TRVs used for wildlife exposure to triclopyr.

The wildlife exposures of highest concern for triclopyr are for small insectivorous birds and mammals. Data are summarized for Probable and Possible exposures below.

1. **A small bird eating contaminated insects (Probable) – triclopyr BEE and triclopyr TEA.** The Central dose estimate for a small bird eating contaminated insects is 1.2 times the TRV. The Upper estimate is 5.2 times the TRV. These values are the same for triclopyr BEE and TEA because the exposure estimate is based on the application rate, and the TRVs are identical for the two chemicals.
2. **A small mammal eating contaminated insects (Probable) – triclopyr BEE and triclopyr TEA.** The Central dose estimate for a small mammal eating contaminated insects is 46% of the TRV. The Upper dose estimate is 2.1 times the TRV. These values are the same for triclopyr BEE and TEA because the exposure estimate is based on the application rate and the TRVs are identical for the two chemicals.
3. **Consumption of contaminated prey by carnivorous mammals or birds, acute (Possible) – triclopyr BEE and triclopyr TEA.** Central estimates of exposures for all carnivorous mammals and birds are less than 10% of the TRVs. The Upper estimate for a carnivorous bird is 15% of the TRV. These values are the same for triclopyr BEE and TEA because the exposure estimate is based on the application rate and the TRVs are identical for the two chemicals.
4. **Drinking water contaminated contaminated by long-term runoff, chronic (Probable) – triclopyr BEE and triclopyr TEA.** None of the hazard quotients for long-term runoff scenarios exceeded 0.30% of any TRV. These estimates account only for the

application rate used and not the acres treated, the effect of buffer zones, or the volume of the water body. These values are the same for triclopyr BEE and TEA because the exposure estimate is based on the application rate and the TRVs are identical for the two chemicals.

Of the Improbable scenarios, 100% absorption of direct spray to 50% of the body emerges as a potentially problematic scenario for bees and small mammals, as HQs exceed one for triclopyr BEE and TEA. Dermal absorption is higher for triclopyr BEE than triclopyr TEA. However, the wildlife accidental spray scenarios assume that 100% of the chemical on wildlife skin or fur is ingested through grooming, which makes this scenario Improbable. Upper estimates of dermal exposures to honeybees and small mammals are 2.7 times the TRV and 73% of the TRV, respectively. Consumption of water after a 20-gallon spill of concentrated Garlon 4 Ultra into a pond produced Upper HQs ranging from 8.3% of the TRV to 60% of the TRV for terrestrial wildlife. The same scenario for Garlon 3A (triclopyr TEA) produces HQs between 0.063 and 0.45. Central acute exposure estimates for large mammals or birds are 34% and 83% of the TRV, respectively. Upper acute exposure estimates are 1.5 times the TRV and 3.5 times the TRV for mammals and birds respectively. Central chronic exposure estimates for large mammals and birds are somewhat higher at 1.01 times the TRV and 79% of the TRV. Upper estimates are also higher, at 19 and 15 times the TRVs.

Table 4-24 summarizes the acute exposure estimates and hazard quotients for terrestrial wildlife exposure scenarios to triclopyr BEE and triclopyr TEA. Table 4-25 summarizes the chronic toxicity of both chemicals. Unlike human RfDs, wildlife TRVs do not include uncertainty factors. If uncertainty factors were applied to the TRVs, hazard quotients would more frequently exceed one.

Aggregate exposure estimates are the sum of dermal and food exposures. Water consumption was not included in aggregate exposure estimates because the only Possible water contamination scenario was long-term runoff, which is anticipated to occur at least several months after the day of a direct spray or consumption of contaminated insects or vegetation. USFS/SERA did not calculate aggregate exposures; this calculation was added for insectivorous and herbivorous small mammals because of their vulnerability to direct sprays and eating contaminated food in a single day. The results are presented in Table 4-26.

Three aggregate scenarios for terrestrial exposure to triclopyr produced hazard quotients for Central exposure estimates greater than 0.1. The Upper estimate for one of these scenarios exceeded an HQ of 1.

1. **Aggregate exposure for a small mammal directly sprayed and eating contaminated fruit**
 - a. **Triclopyr BEE.** The Central HQ for the aggregate exposure for a small mammal eating contaminated fruit was 33% of the TRV. The Upper estimate had an HQ equal to 61% of the TRV. Exposure was dominated by the direct spray scenario, which accounted for 98% of the dose.
 - b. **Triclopyr TEA.** The Central HQ for the aggregate exposure for a small mammal eating contaminated fruit was 17% of the TRV. The Upper estimate had an HQ equal

- to 53% of the TRV. Exposure was dominated by the direct spray scenario, which accounted for 85% of the dose. Because the first order dermal absorption was different between triclopyr BEE and TEA (and 100% absorption due to grooming was not assumed), the exposure estimates were different.
2. **Aggregate exposure for a small mammal directly sprayed and eating contaminated insects.**
 - a. **Triclopyr BEE.** The Central HQ for the aggregate exposure estimate for a small mammal eating contaminated insects was 76% of the TRV. The Upper HQ was 2.7 times the TRV. Both the direct spray and food consumption scenarios contributed substantially to the aggregate dose, with 39% of the Central estimate accounted for by direct spray and 61% accounted for by consumption of contaminated insects.
 - b. **Triclopyr TEA.** The Central HQ for the aggregate exposure estimate for a small mammal eating contaminated insects was 60% of the TRV. The Upper HQ was 2.5 times the TRV. Both the direct spray and food consumption scenarios contributed substantially to the aggregate dose, with 23% of the Central estimate accounted for by direct spray and 77% accounted for by consumption of contaminated insects. Because the first order dermal absorption was different between triclopyr BEE and TEA (and 100% absorption due to grooming was not assumed), the exposure estimates were different.

4.5.5.B Terrestrial Plants

For terrestrial plants, unintended direct spray will result in an exposure equivalent to the application rate. Most plants, with the exception of monocots and conifers, that are sprayed directly with triclopyr at or near the recommended range of application rates will be damaged. Buffer zones of 300 feet or use of protective barriers to prevent spray drift during the application are recommended to protect sensitive plants. Triclopyr is persistent enough and absorbed through the roots sufficiently that there may be some residual herbicidal activity in treated areas. This factor should be accounted for if replanting of native plants is being considered.

Table 4-24: Estimated Acute Triclopyr BEE Exposures and Hazard Quotients for Terrestrial Wildlife

Scenario	Receptor	mg/kg-day or mg/kg/event			TRV (mg/ kg)	Hazard Quotient (HQ)		
		Central	Lower	Upper		Central	Lower	Upper
Direct Spray, formulation specific								
First-order absorption, triclopyr BEE	Small mammal	30	0.16	59	100	0.30	0.0016	0.59
First-order absorption, triclopyr TEA	Small mammal	14	2.7	46	100	0.14	0.027	0.45
Direct Spray, triclopyr BEE and TEA								
100% absorption of direct spray to 50% of body	Small mammal	48	24	73	100	0.48	0.24	0.73
100% absorption of direct spray to 50% of body	Honeybee	320	160	480	179	1.8	0.90	2.7
Consumption of contaminated fruit and vegetation, , triclopyr BEE and TEA								
Fruit	Small mammal	2.50	0.36	8.0	100	0.025	0.0036	0.080
Grass	Large mammal	34	17	150	100	0.34	0.17	1.5
Grass	Large bird	54	27	230	65	0.83	0.41	3.5
Consumption of contaminated water, triclopyr BEE								
20 gal spill of diluted product into pond	Small mammal	0.43	0.11	1.6	100	0.0043	0.0011	0.016
	Large mammal	0.19	0.047	0.71	100	0.0019	0.00047	0.0071
	Small bird	0.78	0.20	2.9	65	0.012	0.0030	0.045
	Large bird	0.11	0.027	0.41	65	0.0017	0.00042	0.0063
20 gal spill of diluted product into reservoir	Small mammal	0.000022	5.4 x10 ⁻⁶	0.000081	100	2.2x10 ⁻⁷	5.4 x10 ⁻⁸	8.1 x10 ⁻⁷
	Large mammal	9.5 x10 ⁻⁶	2.4 x10 ⁻⁶	0.000036	100	9.5 x10 ⁻⁸	2.4 x10 ⁻⁸	3.6 x10 ⁻⁷
	Small bird	0.000040	9.9 x10 ⁻⁶	0.00015	65	6.1 x10 ⁻⁷	1.5 x10 ⁻⁷	2.3 x10 ⁻⁶
	Large bird	5.5 x10 ⁻⁶	1.4 x10 ⁻⁶	0.000021	65	8.5 x10 ⁻⁸	2.1 x10 ⁻⁸	3.2 x10 ⁻⁷
20 gal spill of conc. product into pond	Small mammal	5.3	--	21	100	0.053	^a	0.21
	Large mammal	2.4	--	9.4	100	0.024	^a	0.094
	Small bird	9.8	--	39	65	0.15	^a	0.60
	Large bird	1.4	--	5.4	65	0.021	^a	0.083
20 gal spill of conc. product into reservoir	Small mammal	0.00027	--	0.0011	100	2.7x10 ⁻⁶	^a	0.000011
	Large mammal	0.00012	--	0.00048	100	1.2x10 ⁻⁶	^a	4.8x10 ⁻⁶
	Small bird	0.00050	--	0.0020	65	7.6x10 ⁻⁶	^a	0.000031
	Large bird	0.000069	--	0.00027	65	1.1x10 ⁻⁶	^a	4.2x10 ⁻⁶
Consumption of contaminated fish, triclopyr BEE								
20 gal spill of diluted product into pond	Fish-eating bird	0.24	0.030	1.4	65	0.0037	0.00046	0.021
20 gal spill of diluted product into reservoir	Fish-eating bird	0.000012	1.5x10 ⁻⁶	0.000069	65	1.9x10 ⁻⁷	2.4x10 ⁻⁸	1.1x10 ⁻⁶
20 gal spill of concentrated product into pond	Fish-eating bird	3.0	1.5	18	65	0.046	0.023	0.28
20 gal spill of concentrated product into reservoir	Fish-eating bird	0.00015	0.000076	0.00092	65	2.4x10 ⁻⁶	1.2x10 ⁻⁶	0.000014
Consumption of contaminated insects, triclopyr BEE and TEA								
	Small mammal	46	23	208	100	0.46	0.23	2.1
	Small bird	75	38	338	65	1.2	0.58	5.2

Table 4-24 (cont.): Estimated Acute Triclopyr BEE and TEA Exposures and Hazard Quotients for Terrestrial Wildlife

Scenario	Receptor	mg/kg-day or mg/kg/event			TRV (mg/ kg)	Hazard Quotient (HQ)		
		Central	Lower	Upper		Central	Lower	Upper
Consumption of contaminated water, triclopyr TEA								
20 gal spill of diluted product into pond	Small mammal	0.32	0.080	1.20	100	0.0032	0.00080	0.012
	Large mammal	0.14	0.035	0.53	100	0.0014	0.00035	0.0053
	Small bird	0.59	0.15	2.2	65	0.0091	0.0023	0.034
	Large bird	0.081	0.020	0.31	65	0.0012	0.00031	0.0047
20 gal spill of diluted product into reservoir	Small mammal	0.000016	4.0 x10 ⁻⁶	0.000061	100	1.6x10 ⁻⁷	4.0 x10 ⁻⁸	6.1 x10 ⁻⁷
	Large mammal	7.2 x10 ⁻⁶	1.8 x10 ⁻⁶	0.000027	100	7.2 x10 ⁻⁸	1.8 x10 ⁻⁸	2.7 x10 ⁻⁷
	Small bird	0.000030	7.5 x10 ⁻⁶	0.00011	65	4.6 x10 ⁻⁷	1.2 x10 ⁻⁷	1.7 x10 ⁻⁶
	Large bird	4.1 x10 ⁻⁶	1.0 x10 ⁻⁶	0.000016	65	6.3 x10 ⁻⁸	1.6 x10 ⁻⁸	2.4 x10 ⁻⁷
20 gal spill of conc. product into pond	Small mammal	5.3	--	16	100	0.053	^a	0.16
	Large mammal	2.4	--	7.1	100	0.024	^a	0.071
	Small bird	9.8	--	29	65	0.15	^a	0.45
	Large bird	1.4	--	4.1	65	0.021	^a	0.063
20 gal spill of conc. product into reservoir	Small mammal	0.00027	--	0.00081	100	2.7x10 ⁻⁶	^a	8.1x10 ⁻⁶
	Large mammal	0.00012	--	0.00036	100	1.2x10 ⁻⁶	^a	3.6x10 ⁻⁶
	Small bird	0.00050	--	0.0015	65	7.7x10 ⁻⁶	^a	0.000023
	Large bird	0.000069	--	0.00021	65	1.1x10 ⁻⁶	^a	3.2x10 ⁻⁶
Consumption of contaminated water by peak runoff, triclopyr BEE and TEA								
Peak runoff ^b	Small mammal	0.026	0.00015	0.18	100	0.00026	1.5 x10 ⁻⁶	0.0018
	Large mammal	0.012	0.000065	0.078	100	0.00012	6.5 x10 ⁻⁷	0.00078
	Small bird	0.049	0.00027	0.32	65	0.00075	4.2 x10 ⁻⁶	0.0050
	Large bird	0.0067	0.000037	0.045	65	0.00010	5.7 x10 ⁻⁷	0.00069
Consumption of contaminated fish, triclopyr TEA								
20 gal spill of diluted product into pond	Fish-eating bird	0.18	0.023	1.0	65	0.0028	0.00035	0.016
20 gal spill of diluted product into reservoir	Fish-eating bird	9.2x10 ⁻⁶	1.2x10 ⁻⁶	0.000052	65	1.4x10 ⁻⁷	1.8x10 ⁻⁸	8.0x10 ⁻⁷
20 gal spill of concentrated product into pond	Fish-eating bird	3.0	1.5	14	65	0.046	0.023	0.21
20 gal spill of concentrated product into reservoir	Fish-eating bird	0.00015	0.000076	0.00069	65	2.3x10 ⁻⁶	1.2x10 ⁻⁶	0.000011
Consumption of contaminated small mammal, triclopyr BEE and TEA								
	Carnivorous small mammal	4.20	2.10	6.29	100	0.042	0.021	0.063
	Carnivorous large mammal	2.25	1.12	3.37	100	0.023	0.011	0.034
	Carnivorous bird	6.46	3.23	9.70	65	0.099	0.050	0.15

TRV = Toxicity Reference Value. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are **bolded**.

^a Only two estimates of concentration were calculated for spills of concentrated Garlon 3A product, 33% and 100% of Garlon 3A by volume.

^b Peak runoff was estimated using the USFS worksheets based on application rate [(mg/L)/(lb/acre)] and is not specific to a particular water body. See Section 2.4.2 for more discussion of this topic.

Table 4-25: Estimated Chronic Triclopyr BEE and TEA Exposures and Hazard Quotients for Terrestrial Wildlife

Scenario	Receptor	mg/kg-day or mg/kg-event			TRV (mg/kg)	Hazard Quotient (HQ)		
		Central	Lower	Upper		Central	Lower	Upper
Consumption of contaminated fruit and vegetation								
On-site, fruit	Small mammal	0.12	0.0067	1.1	5	0.024	0.0013	0.22
Off-site, fruit		0.0012	0.000039	0.020	5	0.00025	7.7x10 ⁻⁶	0.0040
On-site, vegetation	Large mammal	5.0	0.65	96	5	1.01	0.13	19
Off-site, vegetation		0.17	0.037	1.80	5	0.034	0.0074	0.36
On-site, vegetation	Large bird	7.9	1.0	150	10	0.79	0.10	15
Off-site, vegetation		0.27	0.059	2.8	10	0.027	0.0059	0.28
Consumption of contaminated water								
Long-term runoff ^a	Small mammal	0.0029	0.000046	0.016	5	0.00058	9.2x10 ⁻⁶	0.0033
Long-term runoff ^a	Large mammal	0.0013	0.000020	0.0072	5	0.00026	4.1x10 ⁻⁶	0.0014
Long-term runoff ^a	Small bird	0.0054	0.000085	0.030	10	0.00054	8.5x10 ⁻⁶	0.0030
Long-term runoff ^a	Large bird	0.00074	0.000012	0.0041	10	0.000074	1.2x10 ⁻⁶	0.00042
Consumption of contaminated fish								
Long-term runoff	Fish-eating bird	0.0017	0.000013	0.014	10	0.00017	1.3x10 ⁻⁶	0.0014

TRV = Toxicity Reference Value. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are bolded.

^a Long-term runoff was estimated using the USFS worksheets based on application rate [(mg/L)/(lb/acre)] and is not specific to a particular water body (see Section 2.4.2).

Table 4-26: Triclopyr BEE and TEA Aggregate Exposures and Hazard Quotients for Terrestrial Wildlife

Animal	Scenario	Exposure Estimates (mg/kg)		
		Central	Lower	Upper
Triclopyr BEE				
Herbivorous small mammal eating fruit (TRV = 100 mg/kg)				
	Direct spray, first order absorption	30	0.16	59
	Eating fruit	2.5	0.36	8.0
	<i>Sum</i>	32.5	0.52	67
	<i>HQ</i>	0.33	0.0052	0.67
Insectivorous small mammal (TRV = 100 mg/kg)				
	Direct spray, first order absorption	30	0.16	59
	Eating insects	46	23	208
	<i>Sum</i>	76	23.2	267
	<i>HQ</i>	0.76	0.23	2.7
Triclopyr TEA				
Herbivorous small mammal eating fruit (TRV = 100 mg/kg)				
	Direct spray, first order absorption	14	2.7	45
	Eating fruit	2.5	0.36	8.0
	<i>Sum</i>	16.5	3.1	53
	<i>HQ</i>	0.17	0.031	0.53
Insectivorous small mammal (TRV = 100 mg/kg)				
	Direct spray, first order absorption	14	2.7	45
	Eating insects	46	23	208
	<i>Sum</i>	60	25.7	253
	<i>HQ</i>	0.60	0.26	2.5

TRV = Toxicity Reference Value. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are **bolded**.

The values summed in this table are taken from Table 4-24.

4.5.5.C Aquatic Wildlife

The calculated water concentrations of triclopyr for aquatic life are the same as those used in the human and terrestrial exposure estimates for drinking water (see Tables 4-14 and 4-15). Acute exposure estimates are compared to TRVs for triclopyr BEE, the active ingredient in Garlon 4 Ultra and triclopyr TEA, the active ingredient in Garlon 3A. For the chronic long-term runoff scenario, the acute TRV for the triclopyr degradation product 3,5,6-trichloro-2-pyridinol (TCP) is used, since triclopyr BEE and triclopyr TEA is transformed into TCP in the environment in the time frame over which long-term runoff might occur.⁹⁵ Although amphibians were not explicitly considered in the SERA/USFS worksheets, tadpoles were added to the risk characterizations and considered with aquatic wildlife.

Exposure scenarios are summarized in Tables 4-27 and 4-28. The only aquatic scenario considered Probable is the long-term runoff scenario. The long-term runoff estimates calculated by the USFS methodology account only for the application rate used and not the acres treated,

the effect of buffer zones, or the volume of the water body. Exposures from this scenario exceed TRVs for triclopyr for the following species in this risk assessment:

1. **Fish**

Triclopyr BEE and TEA. The Upper estimate for fish is 1.5 times the TRV. The Central HQ is 27% of the TRV. Long-term runoff results in the same risk estimates for triclopyr BEE and TEA since they both degrade to TCP; triclopyr BEE and TEA have the same chronic TRV for fish.

2. **Aquatic Invertebrates**

a. **Triclopyr BEE.** The Central HQ for aquatic invertebrates is 8% of the TRV and the Upper HQ is 44% of the TRV.

b. **Triclopyr TEA.** The Central HQ for aquatic invertebrates is 7.9% of the TRV and the Upper HQ is 44% of the TRV.

3. **Aquatic Plants**

a. **Triclopyr BEE.** The Central HQ for aquatic plants is 29% of the TRV. The Upper estimate for aquatic plants is 1.6 times the TRV.

b. **Triclopyr TEA.** The Central HQ for aquatic plants is 2.9% of the TRV. The Upper estimate for aquatic plants is 16% of the TRV.

For the long-term runoff scenario envisioned for the MMWD watershed, the triclopyr TEA estimate is most relevant, since the BEE will have degraded to triclopyr acid. Further degradation to TCP also occurs; however, no data were available on the toxicity of TCP to plants. It is assumed to be less active as an herbicide, compared to triclopyr acid.

Concentration estimates for triclopyr BEE and TEA are the same for all long term runoff scenarios because the two chemicals have the same water contamination rates, based on triclopyr acid.

The highest hazard quotients calculated were for the Highly Improbable spills of concentrated triclopyr products into a small, thermally stratified pond, with all Central HQs for 20 gallon spills exceeding a value of at least 5.4 (tadpoles). The highest Central HQ is 2,800 times the TRV for fish. Upper HQs are substantially higher. MMWD should do everything possible to minimize the potential for an acute spill of triclopyr near water bodies.

We conclude that if substantial amounts of triclopyr are to be used on MMWD land, it is possible that aquatic life will be adversely affected. Risks to aquatic life could be reduced by restriction of the use of triclopyr to very small treatment areas distant from water bodies.

A realistic model for the effects of triclopyr on aquatic species would also account for population-level effects of herbicides related to trophic interactions (food webs). Aquatic plants, especially algae, are the foundation of the food web and are also one of the most sensitive species to triclopyr. Declines in the population of algae and macrophytes may have consequences for aquatic herbivores and the species that depend on them for sustenance. If use of triclopyr is limited to spot treatments on few acres, runoff in amounts that would cause population effects is unlikely.

Table 4-27: Estimated Triclopyr BEE Hazard Quotients for Aquatic Wildlife

Receptor	Scenario	Hazard Quotients			TRV (mg/L)
		Central	Lower	Upper	
Fish					
Spill of diluted product into pond	1 gal	11	3	42	0.013
	20 gal	220	56	840	0.013
Spill of diluted product into reservoir	1 gal	0.00057	0.00014	0.0021	0.013
	20 gal	0.011	0.0028	0.043	0.013
Spill of concentrated product into pond	1 gal	140	^a	560	0.013
	20 gal	2,800	^a	11,000	0.013
Spill of concentrated product into reservoir	1 gal	0.0071	^a	0.028	0.013
	20 gal	0.14	^a	0.57	0.013
Peak runoff ^b		14	0.077	92	0.013
Long-term runoff ^{b, c}		0.27	0.0042	1.5	0.075
Amphibians (Tadpoles)					
Spill of diluted product into pond	1 gal	0.022	0.0054	0.081	6.7
	20 gal	0.43	0.11	1.63	6.7
Spill of diluted product into reservoir	1 gal	1.1x10 ⁻⁶	2.7x10 ⁻⁷	4.2x10 ⁻⁶	6.7
	20 gal	0.000022	5.5x10 ⁻⁶	0.000082	6.7
Spill of concentrated product into pond	1 gal	0.27	--	1.1	6.7
	20 gal	5.4	--	22	6.7
Spill of concentrated product into reservoir	1 gal	0.000014	--	0.000055	6.7
	20 gal	0.00027	--	0.0011	6.7
Peak runoff ^b		0.027	0.00015	0.18	6.7
Long-term runoff ^b		0.017	0.00028	0.092	1.2
Aquatic Invertebrates					
Spill of diluted product into pond	1 gal	0.20	0.049	0.74	0.74
	20 gal	3.93	0.99	14.9	0.74
Spill of diluted product into reservoir	1 gal	0.00001	2.4x10 ⁻⁸	0.000038	0.74
	20 gal	0.00020	0.000050	0.00076	0.74
Spill of concentrated product into pond	1 gal	2.43	--	0.99	0.74
	20 gal	48.6	--	203	0.74
Spill of concentrated product into reservoir	1 gal	0.00012	--	0.00050	0.74
	20 gal	0.0024	--	0.0097	0.74
Peak runoff ^b		0.24	0.0014	1.62	0.74
Long-term runoff ^{b, c}		0.080	0.00132	0.44	0.25
Aquatic Plants					
Spill of diluted product into pond	1 gal	2.1	0.52	7.8	0.07
	20 gal	42	10.4	156	0.07
Spill of diluted product into reservoir	1 gal	0.00011	0.000026	0.00040	0.07
	20 gal	0.0021	0.00053	0.0079	0.07
Spill of concentrated product into pond	1 gal	26	^a	104	0.07
	20 gal	520	^a	2070	0.07
Spill of concentrated product into reservoir	1 gal	0.0013	^a	0.0053	0.07
	20 gal	0.026	^a	0.10	0.07
Peak runoff ^b		2.6	0.014	17	0.07
Long-term runoff ^b		0.29	0.0045	1.6	0.07

TRV = Toxicity Reference Value. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are bolded.

^a Only two estimates of concentration were calculated for spills of concentrated Garlon 4 Ultra product, 25% and 100% of Garlon 4 Ultra by volume.

^b Peak and long-term runoff were estimated using the USFS worksheets based on application rate [(mg/L)/(lb/acre)] and are not specific to a particular water body. See Section 2.4.2 for more discussion of this topic.

^c Long-term runoff risk calculations for triclopyr BEE and TEA utilize the TRV for TCP, since this is the predominant species present under the long-term runoff scenario.

Table 4-27: Estimated Triclopyr TEA Hazard Quotients for Aquatic Wildlife xxx

Receptor	Scenario	Hazard Quotients			TRV (mg/L)
		Central	Lower	Upper	
Fish – Triclopyr TEA					
Spill of diluted product into pond	1 gal	0.0011	0.00026	0.0039	104
	20 gal	0.021	0.0052	0.079	104
Spill of diluted product into reservoir	1 gal	5.3x10 ⁻⁸	1.4x10 ⁻⁸	2.0x10 ⁻⁷	104
	20 gal	1.1x10 ⁻⁶	2.7x10 ⁻⁷	3.9x10 ⁻⁶	104
Spill of concentrated product into pond	1 gal	0.018	^a	0.053	104
	20 gal	0.35	^a	1.0	104
Spill of concentrated product into reservoir	1 gal	8.9x10 ⁻⁷	^a	2.7x10 ⁻⁶	104
	20 gal	0.000017	^a	0.000053	104
Peak runoff ^b		0.0017	9.6 x10 ⁻⁶	0.012	104
Long-term runoff ^{bc}		0.27	0.0041	1.5	0.075
Amphibians (Tadpoles)					
Spill of diluted product into pond	1 gal	0.016	0.0040	0.061	6.7
	20 gal	0.33	0.081	1.2	6.7
Spill of diluted product into reservoir	1 gal	8.2x10 ⁻⁷	2.1x10 ⁻⁷	3.1x10 ⁻⁶	6.7
	20 gal	0.000016	4.2x10 ⁻⁶	0.000061	6.7
Spill of concentrated product into pond	1 gal	0.27	--	0.82	6.7
	20 gal	5.4	--	16	6.7
Spill of concentrated product into reservoir	1 gal	0.000014	--	0.000042	6.7
	20 gal	0.00027	--	0.0008	6.7
Peak runoff ^b		0.027	0.00015	0.18	6.7
Long-term runoff ^{bc}		0.017	0.00028	0.092	1.2
Aquatic Invertebrates					
Spill of diluted product into pond	1 gal	0.011	0.0028	0.043	9.67
	20 gal	0.23	0.056	0.84	9.67
Spill of diluted product into reservoir	1 gal	5.70 x10 ⁻⁷	1.44E-07	2.16 x10 ⁻⁶	9.67
	20 gal	1.14 x10 ⁻⁵	2.88E-06	4.20 x10 ⁻⁵	9.67
Spill of concentrated product into pond	1 gal	0.19	^a	0.57	9.67
	20 gal	3.72	^a	11.40	9.67
Spill of concentrated product into reservoir	1 gal	9.60x10 ⁻⁶	^a	2.88x10 ⁻⁵	9.67
	20 gal	0.00019	^a	0.00057	9.67
Peak runoff ^b		0.019	0.00010	0.13	9.67
Long-term runoff ^{bc}		0.079	0.0012	0.44	0.25
Aquatic Plants					
Spill of diluted product into pond	1 gal	0.16	0.39	0.58	0.7
	20 gal	3.1	0.78	12	0.7
Spill of diluted product into reservoir	1 gal	7.9x10 ⁻⁶	2.0x10 ⁻⁶	0.000030	0.7
	20 gal	0.00016	0.000040	0.00059	0.7
Spill of concentrated product into pond	1 gal	2.6	^a	7.9	0.7
	20 gal	52	^a	156	0.7
Spill of concentrated product into reservoir	1 gal	0.00013	^a	0.00040	0.7
	20 gal	0.0026	^a	0.079	0.7
Peak runoff ^b		0.26	0.0014	1.7	0.7
Long-term runoff ^b		0.029	0.00044	0.16	0.7

TRV = Toxicity Reference Value. Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are bolded.

^a Only two estimates of concentration were calculated for spills of concentrated Garlon 4 Ultra product, 25% and 100% of Garlon 4 Ultra by volume.

^b Peak and long-term runoff were estimated using the USFS worksheets based on application rate [(mg/L)/(lb/acre)] and are not specific to a particular water body. See Section 2.4.2 for more discussion of this topic.

^c Long-term runoff risk calculations for triclopyr BEE and TEA utilize the TRV for TCP, since this is the predominant species present under the long-term runoff scenario.

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