Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides

Volume 5

TRICLOPYR

Study No. 00713

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Ecology is making this risk assessment available as it was submitted on March 21, 2001, from Compliance Services International due to public demand. The risk assessment has not been edited or updated to reflect EPA's most recent registration information on triclopyr. Ecology's Environmental Impact Statement (publication 04-10-018), which is based in part on this supporting information, does reflect the updated EPA assessment. EPA's assessment is available on-line at: http://cfpub.epa.gov/oppref/rereg/status.cfm?show=rereg#T.

Any comments or questions concerning the data in this document should be directed to Compliance Services International, 1112 Alexander Avenue, Tacoma, WA 98421, or call 253-272-6345.

Supplemental Environmental Impact Statement
Assessments of Aquatic Herbicides

Triclopyr

Volume 5, Section 1

LABEL DESCRIPTION & HISTORY

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1.0 REGISTRATION STATUS

This section describes the historic and current Federal labels and use directions. It also summarizes application rates and weeds controlled, as well as reporting on typical practices undertaken by licensed Washington applicators. The final section describes research underway, including rate and application technology and proposed new labeling.

1.1 TRICLOPYR AS AN AQUATIC HERBICIDE

1.1.1 Registration Requirements

In order to register a pesticide with the EPA for use in the United States, the active ingredient and its formulations must be tested for physical chemistry, mammalian toxicity, environmental fate, effects on ground water, and eco-tox effects. Work must also be done to demonstrate the expected magnitude of residue on edible products and residues in water. After this data is generated, it is submitted to various branches of EPA for review. If EPA finds that the product does not pose significant risk to man, livestock, or wildlife and has a favorable environmental persistence and degradation profile, a registration will be granted. With that registration, the manufacturer has permission to sell the product in the United States. However, each state may have its own separate registration process which may be more stringent than the EPA's registration process.

Washington State's registration procedure follows the EPA registration: It requires that the applicant submit a copy of the EPA approved label and a copy of the confidential statement of formula. The Washington State Department of Agriculture reviews these submittals for compliance with state and Federal requirements. If these requirements are filled, the product will be registered by the state unless it presents an unusual hazard to the environment.

Studies conducted for submission to EPA since 1987 must be conducted in compliance with Good Laboratory Practice (GLP) regulations as specified in 40 CFR (Code of Federal Regulations) 160. These regulations were designed to improve the quality of record keeping and to prevent fraud. They specify what records must be kept and how long they must be kept. They also specify how long analytical standards must be kept, how often they must be re-characterized and storage conditions. Furthermore, they provide guidelines on how to determine the length of time that organic and inorganic reagents, solvents and biological samples can be kept, and under what conditions they should be stored. Also, GLPs provide guidance on how the integrity of the biological samples can be determined. For practical purposes, GLPs insures the integrity of the data. They allow for the reconstruction and interpretation of data within the study.

There are no products containing triclopyr currently approved for aquatic use. The Washington State Department of Ecology ("Ecology") has an interest in the use of the product Renovate® Specialty Herbicide (SEPRO Corporation) or Garlon® 3A Specialty Herbicide (Dow AgroSciences) for the control of target nuisance aquatic and wetland plants in lakes, ponds, reservoirs, marshes, wetlands and the banks and shores of these sites. This product is available under an Experimental Use Permit (EUP) and is expected to receive full registration by the third quarter of 2000. Renovate® Specialty Herbicide contains 44.4% triclopyr TEA (triethylamine) as the active ingredient (31.8% = 3.00 pounds triclopyr acid equivalent/gallon). There are no registered aquatic uses for triclopyr TEA at this time. Triclopyr triethylamine salt (TEA) initially received Federal registration for control of broadleaf weeds and woody plants in 1979. Triclopyr butoxyethyl ester (BEE) was subsequently registered in 1979 for use on the same sites. Both formulations were registered for use on turf sites in 1984. In 1985, triclopyr BEE was registered for use on rangeland and permanent grass pastures. In 1995, triclopyr TEA was registered for use on rice to control many hard to control broadleaf weed species. The Reregistration Eligibility Decision (RED) process for triclopyr acid, triclopyr TEA and triclopyr BEE was completed on September 30, 1997. Triclopyr TEA is effective against Eurasian watermilfoil (*Myriophyllum spic*atum), purple loosestrife (*Lythrum salicaria)*, water hyacinth (*Eichhornia crassipes*) and alligatorweed *(Alternanthera philoxeroides*) and other species specified in the label. However, pondweed species (e.g., *Potamogeton zosteriformis*), rushes (*Scirpus* spp.), cattails (*Typha* spp.), coontail (*Ceratophyllum demersum*) duckweed (*Lemna* spp.) and various algae species are not typically controlled at the maximum labeled concentration of 2.5 ppm a.e. Triclopyr TEA is also effective in controlling wetland associated plants including many woody plants and annual or perennial broadleaf weeds. Wetland sites include flood plains, deltas, marshes, swamps, bogs and transitional areas between upland and lowland sites. These wetlands may occur in forests, non-crop sites, wildlife habitat restoration and management areas and areas adjacent to or surrounding domestic water supply reservoirs, lakes and ponds.

1.1.2 1992 Environmental Impact Statement and Effects of State Senate Bill 5424

In the State of Washington, all applications of aquatic herbicides and algaecides are performed under a state permit system. Ecology manages this system and uses a 1992 Environmental Impact Statement (EIS) for diquat, copper compounds, glyphosate, endothall and fluridone as well as manual, mechanical and biocontrol methods as its basis for writing permits for aquatic weed and algae control in this state (Ecology, 1992). The State permitting system is a result of six agencies working together to develop a statewide integrated pest management system for aquatic plants and noxious emergent vegetation. The goal of this system is to ensure that the most effective and least environmentally damaging management alternatives will be used.

Triclopyr triethylamine salt (triclopyr (TEA) as Garlon® 3A Specialty Herbicide (44.4% a.i = 31.8% a.e.) from Dow AgroScience LLC or Renovate® Specialty Herbicide (44.4% a.i. = 31.8% a.e.) from SEPRO Corporation are proposed for registration by EPA for national use. However, a label for the current aquatic and wetland uses has not yet been issued. Therefore, triclopyr TEA is currently being used by the State of Washington under an experimental use permit; and in the future it may be registered in the State of Washington for the control of aquatic weeds in public water ways, annual and perennial broadleaf weeds and woody brush in wetlands where use of these products may impact public waterways.

Ecology is responsible for issuing short-term modifications (STMs) to the water quality standards. These are required for management activities such as use of pesticides, mechanical, or other control methods that might cause excess turbidity or violate other provisions of the water quality standards. Ecology is also responsible for ensuring consistency of proposals with rules and regulations designed to protect groundwater, shorelands, wetlands, air quality, and other elements of the environment.

In 1999, the Washington State Legislature passed legislation (ESBB 5424) requiring an update to the 1992 EIS. From 1992 to present, there has been a considerable amount of research done to support the continuing registration of aquatic herbicides and algaecides. As such, the most current data for these materials has not been considered or used in the issuance of permits to perform aquatic weed and algae control in Washington State (Resource Management, Inc., 1999).

Renovate® Specialty Herbicide (triclopyr TEA) is available under an Experimental Use Permit (EUP). Under the EUP Renovate® may be used to control woody plants and certain annual or perennial weeds in ponds, lakes reservoirs, marshes and wetlands, and the banks and shores of these sites. The proposed Garlon® 3A label specifies a number of full or partial aquatic species that may be controlled by triclopyr TEA including Eurasian water milfoil (*Myriophyllum spicatum*), American lotus (*Nelumbo lutea*), parrotfeather (*Myriophyllum aquaticum*), pennywort (*Hydrocotyle* spp.), waterhyacinth (*Eichhornia crassipes*), waterlilies (*Nymphaea od*orata and *Nuphar* spp.), waterprimrose (*Ludwigia uruguayensis*), alligatorweed (*Alternanthera philoxeroides*) and purple loosestrife (*Lythrum salicaria*). Efficacy is also claimed on a variety of wetland associated terrestrial plants like bindweed (*Convolvulus* spp.), Canada thistle (*Circium arvense*), dandelion (*Taraxacum offici*nale), plantain (*Plantago* spp.), ragweed (*Ambrosia* spp.), vetch (*Vicia* spp.) and wild lettuce (*Lactuca* spp.). Other species of wetland associated plants and woody brush may also me controlled. Triclopyr TEA is licensed under Dow AgroSciences and is expected to receive full registration by the third quarter of 2000. Triclopyr TEA for aquatic use will be distributed by Dow AgroSciences and SEPRO Corporation under the Garlon® 3A and Renovate® labels, respectively. Triclopyr TEA and triclopyr acid are practically non-toxic to fish and aquatic invertebrates and are not anticipated to be an acute or chronic risk due to their fairly short half-life (typically <5 days), low intrinsic toxicity to animals and low tendency to bioaccumulate in animal tissue.

Triclopyr TEA has a 96-hour LC50 of 115-357 ppm a.i. (82–256 ppm a.e.) for rainbow trout, 120-613 ppm a.i. (86 –439 ppm a.e.) for fathead minnow and 225-640 ppm a.i. (147-413 ppm a.e.) for bluegill sunfish. Triclopyr TEA has a 48-hour LC50 to *Daphnia magna* of 501-525 ppm a.i. (360-376 ppm a.e.) and a 96-hour LC50 of 58, 326, 392 and >438 ppm a.i. (34, 234, 281, and >314 ppm a.e.) for eastern oyster, grass shrimp, pink shrimp and fiddler crab (estuarine invertebrates), respectively (Section 4, Tables 1, 2, 17 and 18). Since triclopyr TEA is the only product scheduled for aquatic use, products containing this ingredient (Garlon® 3A and Renovate®) are the only products on which risk assessment and a detailed toxicity evaluation will be conducted.

Triclopyr acid has been reported to be practically non-toxic to rainbow trout (LC50 = 117 ppm a.e. for rainbow trout) and bluegill sunfish (96-hour LC50 of 148 ppm a.e.) (Section 4, Tables 2, 17 and 18). Other authors have reported triclopyr acid to be moderately toxic with 96-hour LC50s ranging from 5.3 ppm a.e. for pink salmon (*Oncorhynchus gotbuscha*) to 9.6 ppm a.e. for Chinook salmon *(Oncorhynchus tshawytscha*). Although little work has been done on triclopyr acid with invertebrates, the LC50 for *Daphnia magna* is 132 ppm a.e., which classifies triclopyr acid as practically nontoxic for this species. Triclopyr acid is the conjugate base of triclopyr TEA. However, since the dissociation constant of triclopyr acid is equal to 2.68, it is unlikely that fish or aquatic invertebrates will be exposed to triclopyr acid at significant concentrations in the environment. There are currently no products containing triclopyr acid as the active ingredient. However, information on the toxicity of triclopyr acid can serve as supplementary material to indicate the risk of triclopyr exposure in the aquatic environment.

Formal reports to the EPA by the registrant (Dow Elanco), peer reviewed literature, the EPA RED (1998) and various EPA databases (Brian, 1999 and Ecotox, 2000) were reviewed in order to prepare this risk assessment: 1) The documents used by the registrant to support registration were those documents submitted to EPA in the course of the registration and re-registration process for triclopyr TEA. They were conducted according to the EPA's current pesticide assessment guidelines; if they were conducted after 1987, they were also conducted under Good Laboratory Practice Regulations (40 CFR 160). 2) The bulk of the reviewed literature is fairly recent (published within the last 10 years) and is supported by unpublished literature by the same authors. Much of this data has gone through both the EPA and scientific peer review process. 3) EPA's Brian database contains triclopyr data that supports the submitted regulatory documents. 4) The EPA's ECOTOX database, which is a compilation of ecotoxicology data currently in use at EPA to generate and support ecological risk assessments, contains many references of use for risk assessment. The only general review article available for triclopyr was the EPA RED (1998). The data included in this review includes data on toxicity and environmental fate and risk assessment for triclopyr TEA, triclopyr butoxyethyl ester and triclopyr acid. Where possible, the toxicity values reported in the review articles were verified in the originally cited articles. Unfortunately, many of the values presented in the EPA RED (1998) appear to be incorrect; these ppm values were often reported as active ingredient equivalents when the original documents reported these ppm values in formulation equivalence.

1.1.3 Risk Assessment (For a more detailed analysis see Section 4.1.10.2.5)

Herbicides used for aquatic weed control fall into one or more general categories: 1) Contact herbicides are chemicals that control weeds by direct contact with the foliage and destroy only those portions of the plant (generally the roots survive and plants regrow). 2) Systemic herbicides are applied to the foliage and/or stems of the plant and translocated to the roots or other portions of the plant, eventually resulting in the death of the entire plant. 3) Broad-spectrum herbicides kill most, if not all plants, if the dosage is appropriate. 4) Broadleaf herbicides generally kill dicot plants with broad leaves but there are exceptions; some broadleaf herbicides can kill monocots with broad leaf morphology and certain "narrowleaf" dicots are not harmed at concentrations that typically kill broadleaf plants. 5) Submerged (submersed), emerged (emersed) or floating indicates the way the plant typically grows. i.e., below the water line (submerged), from below the water line to above the waterline (emerged) and on the surface of the water and often un-rooted (floating). Pre-emergent and Post-emergent weed control refers to whether control measures are taken prior to or after germination or first growth of the plant.

Triclopyr is a post-emergent systemic herbicide used primarily to control wetland associated annual and perennial plants and woody brush. However, efficacy has been claimed for a variety of fully or partially aquatic plants including American lotus (*Nelumbo lutea*), Eurasian watermilfoil (*Myriophyllum spicatum*), parrotfeather (*Myriophyllum aquaticum*), pennywort (*Hydrocotyle* spp.), waterhyacinth *(Eichhornia crassipes*), water lilies (*Nuphar* spp. and *Nymphaea odorata*) and waterprimrose (*Ludwigia uruguayenis*), alligatorweed (*Alternanthera philoxeroid*es) and purple loosestrife (*Lythrum salicaria*). The mode of action for triclopyr is as an auxin-like growth hormone which interferes with proper growth (very similar to the mode of action of 2,4-D). Triclopyr is not typically used for algae control and most species of algae are not affected strongly by triclopyr (Section 4, Tables 2, 11 and 16). Many species of native plants are not affected by triclopyr or are not affected except transitorily. Some of these may include pondweed species and coontail, rushes and cattails (Petty et al, 1998). However, at higher use rates (2.5 ppm a.e.), the more susceptible native species such as coontail, Southern naiad and American waterweed may be reduced in numbers in some treatment situations.

The Risk Assessment in Section 4 indicates that triclopyr (triclopyr TEA) may be used safely at concentrations up to 2.5 ppm a.e. when most species of fish and invertebrates are present. The 96-hour LC50 for all verified studies on fish is greater than 82 ppm a.e. Therefore, the Risk Quotient for the most sensitive species of fish is below the acute levels of concern (0.1) for protection of the biota. The Acute Risk Quotient for triclopyr TEA using rainbow trout (*Oncorhynchus mykiss*) is 0.03 (2.5 ppm a.e./82 ppm a.e.). The most sensitive invertebrate are eastern oyster embryos and larvae, (LC50 >18 / <27 ppm a.e.). Therefore, the risk quotient will be at approximately the level of concern for this species if degradtation is not taken into account (RQ = 0.11 = 2.5 ppm a.e./22 ppm a.e). If the longest measured half-life of 7.5 days for triclopyr TEA is considered, the RQ will be at the level of concern (RQ = 0.10 = 2.3 ppm a.e./22 ppm a.e.). Therefore, both fish and aquatic invertebrate biota should not be at high risk from the use of triclopyr TEA to control aquatic weeds. However, since the risk quotient for the most sensitive invertebrates is at the low level of concern, placing triclopyr TEA in the restricted use category may be necessary to prevent any significant impact on these more sensitive invertebrate species.

Use of triclopyr at 6 or 9 lbs a.e./acre to control weeds in non-agricultural uncultivated areas can result in a peak EEC 0.185 and 0.273 ppm a.e., respectively in adjacent water bodies. Since these concentrations are well below the LC50/EC50 of the most sensitive species of fish (82 ppm a.e.) or invertebrate (22 ppm a.e.), the use of triclopyr to control weeds on non-agricultural uncultivated wetland areas should not result in adverse impact to aquatic animals.

Very little chronic testing has been done with triclopyr TEA. However, the data indicates a lack of chronic toxicity for both fathead minnow and *Daphnia magna*. For example, the acute 96-hour LC50 for fathead minnow is 86 to 176 ppm a.e. while the chronic 31-day LC50 for this species is 52-81 ppm a.e. and the MATC = 41 ppm c.e. The 48-hour LC50 for *Daphnia magna* is 360 to 376 ppm a.e. and the 21-day LC50 = 367 ppm a.e. and the 21-day MATC is 35 ppm a.e. Since the chronic risk assessment is less than the chronic level of concern of <1.0 (RQ = 2.5 ppm a.e./41 ppm a.e. for fathead minnow and 2.5 ppm a.e./35 ppm a.e. for *Daphnia magna*), the fish and invertebrate biota are not likely to be adversely affected in their reproductive success when triclopyr TEA is used to control aquatic weeds. This conclusion of no adverse impact is also reached when triclopyr TEA is used to control weeds on non-agricultural uncultivated areas (RQ = 0.01 =0.273 ppm a.e./35 ppm a.e.).

For fish and commercially important invertebrates, the results of acute risk assessments have been confirmed by at least one field study in Lake Minnetonka, Minnesota (Petty et al, 1998). During a 28-day period when fish, crayfish and clams were exposed to an initial concentration of 2.5 ppm c.e., less than 11 percent of caged sentinel organisms died. Between 5 and 11 percent of bluegill sunfish and largemouth bass died during the 28-day exposure period and none of the black bullhead, crayfish or freshwater clams died during this period. The mortalities that occurred during the exposure period were not believed to be due to the direct effect of triclopyr TEA, but an oxygen slump caused by heavy growth of non-target macrophytes. The effects of chronic exposure were not determined in this experiment. However, due to a lack of increased mortality during long exposures, chronic toxicity effects are not believed to be a serious issue during the aquatic use of Triclopyr TEA.

In wetlands where triclopyr TEA was used to control purple loosestrife at tank mix rates of 6% formulated product plus 0.5% LI700® nonionic surfactant, none of the sampled invertebrate species was adversely impacted. Species in the classes Brachiopoda, Copeoda, Ostacoda and Arachnida were not adversely impacted with respect to numbers or diversity at one or seven days post treatment. However, the numbers of Branchipods and Copepods increased significantly over the control at seven days post treatment. In sediment core samples, there were no significant changes in the numbers of the most common taxa at both 1 and 7 days post treatment. The most common taxa seen in Moses Lake sediment were Amphipoda, Diptera and Odonata (Gardner and Grue, 1996). Caged sentinel organisms including rainbow trout, *Daphnia magna* and the macrophyte *Lemna gibba* were not adversely impacted by the use of triclopyr TEA to control purple loosestrife. There was no significant mortality for *Daphnia magna* or rainbow trout in either control or triclopyr TEA treated wetland plots. The number of fronds on the sentinel *Lemna gibba* plants did not vary significantly between the controls and the herbicide treated sites at either 24 or 48 hours post-treatment. Since the chronic toxicity of triclopyr TEA appears to be low, it is unlikely that longer observation periods will produce greater mortality or reduction in numbers of sentinel or *in situ* speicies.

No investigations have been done concerning the smoltification of salmon with triclopyr TEA. However, the very low toxicity of triclopyr TEA on salmonids (96-hour LC50 = 96 to 182 ppm a.e. (Wan et al, 1987) make it unlikely that these or other andromonous species will be adversely impacted. There is no reason to assume that salmonids will exhibit signs of chronic toxicity when the standard species used in chronic tests do not.

Some concern has been expressed concerning the acute and chronic toxicity of the main triclopyr TEA metabolites, TCP (3,5,6-trichloro-2-pyridinol-2) and TMC (2-methoxy-3, 5,6-trichloropyridine. Although the concentrations of these metabolites have not been seen in Lake Seminole at concentrations of higher than ~0.1 ppm, the acute toxicity of these metabolites are much higher than triclopyr TEA. The 96-hour LC50s for these metabolites have been seen to be as low as 1.1 ppm in salmonids for TMP and 1.5 ppm in salmonids for TCP. Although these metabolites are classified as moderately toxic, they are unlikely to cause adverse impact on the fish biota (Wan et al, 1987 and EPA, RED, 1998) since the LC50s are more than ten-fold higher than the time weighted environmental concentration at any exposure period. Similar observations have been made concerning the invertebrate biota. Since the TCP is persistent (half-life = >4-days) in the water column, and the concentration of TCP is likely to exceed 0.01 ppm, freshwater early life-stage studies should be conducted with rainbow trout or Chum or Coho salmon, which have shown acute sensitivity to this metabolite.

Species of aquatic invertebrates that were tested as caged sentinel organisms in the field did not show mortality at exposure periods of 28 days after an initial application of triclopyr TEA at concentrations of 2.5 ppm a.e. After 28-days of exposure, crayfish and freshwater clams displayed no mortality in Lake Minnetonka when it was treated with triclopyr TEA to control Eurasian watermilfoil (Petty et al, 1998). It was also noted by Foster et al (1997) that indigenous populations of macro-invertebrates that were found in ponds located in California, Missouri and Texas were largely unaffected by the direct affects of triclopyr at 2.5 ppm a.e.

Triclopyr TEA appears to be safe to fish, invertebrates, algae and many species of native aquatic macrophytes for use in controlling aquatic and wetland weeds. However, accidental direct over-spray to water bodies containing these organisms may kill or cause adverse impact to the more sensitive species. Direct over-spray of triclopyr TEA at 6 or 9 lbs a.e./acre to 6 inches of water produces peak EECs of 4.4 to 6.6 ppm a.e. Such accidental exposures would result in 4-day time weighted average EEC values of 5.5 to 5.5 ppm a.e. While these concentrations would not harm the fish biota, it is anticipated that the low level of concern for invertebrates would be exceeded (RQ =0.25 = 3.7 ppm a.e./22 ppm a.e.). However, since the high level of concern would not be exceeded, the classification of triclopyr TEA as a restricted use herbicide and application by licensed applicators should prevent adverse impact on the invertebrate biota. The more sensitive plant and algal biota may be adversely impacted by such accidental exposures to triclopyr TEA since the level of concern (1.0) will be exceeded for more sensitive algal species (RQ = 1.30 = 5.5 ppm a.e./4.2 ppm a.e).

1.1.4 Registration Labels

1.1.4.1 Current Labels

There are currently no labels for triclopyr TEA registered in the State of Washington for the control of aquatic weeds and wetland associated weeds. However, Garlon® 3A from Dow AgroSciences and Renovate® from SEPRO Corporation are scheduled for federal registration sometime in the fourth quarter of the year 2000. Renovate® has been used in the State of Washington under an EUP for the control of Eurasian watermilfoil (*Myriophyllum spicatum*) and purple loosestrife (*Lythrum salicaria*) at Loon Lake and Okanogan River floodplain, respectively (Washington State EUP, 1998 to 2000). Control of Eurasian watermilfoil has been shown to be effective in Lake Minnetonka, Minnesota (Getsinger et al, 1998). Triclopyr TEA was also effective in the control of purple loosestrife at Moses Lake during the 1993 season but significant re-growth had returned by the end of the 1994 season (Gardner and Grue, 1996).

However, the current Experimental Use Label for Renovate® indicates that this product may be applied to public waters in ponds, lakes, reservoirs, marshes, and wetlands, including the banks and shores within and adjacent to these sites. The proposed label amendment for Garlon® 3A, indicates that this product may also be used for control of woody plants and broad leaf weeds in forests, terrestrial non-crop sites, industrial sites, rights-of-way, fence rows, non-irrigation ditch banks and around buildings including applications to grazed areas and for establishment and maintenance of wildlife openings within these sites. The proposed labels for these products does not permit their application to saltwater bays or esturaries, flowing water, ditches or canals used to transport irrigation water.

Personal communications from DowElanco's Robert Peterson (2000) indicate that Garlon® 3A should not be used to treat waters that will be used for irrigation within 120 days of the day of treatment. However, if laboratory analysis indicates that the triclopyr concentration in intake water has dropped below the limit of detection, treated water may be used for irrigation. The label restricts use to non-irrigation situations for applications to ditches and/or canals.

It has also been proposed as part of the tolerance petition, that the potable water setback be 0.25 miles in order to ensure residue levels remain below 0.5 ppm (proposed allowable drinking water tolerance). This set back distance was based on the results of several field dissipation studies (Woodburn, 1988 Houtman et al, 1997, Foster et al, 1997). However, recent modeling work (Ritter and Peacock, 2000) indicates that the setback distance should vary with the concentration used and the number of acres treated. At the maximum use rate (2.5 ppm) used to treat $\geq$16 acres, the set back distance from potable water intakes should be at least 2000 feet.

There is currently no proposed restriction on the use of treated water for watering livestock. The proposed tolerance on grass and hay used for feeding livestock is 500 ppm a.e., and the potable water tolerance and maximum treatment rate in water is 0.5 and 2.5 ppm a.e., respectively. Because of the ~1000-fold difference in proposed feed and potable water tolerances, it is expected that the impact on animal health and potential residues in meat and milk would be negligible.

There are no proposed restrictions on the recreational use of water in the treatment area. Water in the treatment area may be used for swimming and fishing immediately after treatment with Garlon® 3A or Renovate®. However, the experimental label indicates that swimming should not be allowed for 24 hours after application. Fishing should not be allowed for 30 days after application according to the Experimental Use label. The harvesting of shellfish (bivalves and crayfish) should not be allowed for 15 days after application.

DowElanco currently manufactures and distributes Garlon® 3A and SEPRO Corporation will market and distribute Renovate® under a separate label. The products will be the same since DowElanco will manufacture both products. There are other triclopyr products including Cool Power® Selective Herbicide, Horsepower® Granular Weed Killer, Horsepower® Selective Herbicide, Horsepower® Spot Weed Killer, Turflon II® Amine, XRM-5202® Premium Granular Weed Killer, XRM-5202® Premium Selective Weed Killer, XRM-5202® Premium Spot Weed Killer and Garlon® 4. All of these products except Garlon® 4 are distributed by Riverdale Chemical. Garlon® 4 is manufactured and distributed by Dow AgroScience. However, these products are not currently labeled for the control of aquatic weeds or wetland associated weeds and brush.

1.1.4.2 Historical Labels

There are no historical labels that include aquatic uses for Garlon® 3® or Renovate®. However, the Experimental Use label for Renovate® and the proposed label for Garlon® 3A are located in Appendix 1 and 2, respectively. These labels do not differ substantially from each other in their proposed uses and restrictions. However, the proposed label expands the irrigation restriction from 14 to 120 days. The proposed potable water restriction changes the set back distance from 1-mile to a maximum of 2000 feet. The potable water use restriction of 21 days for water taken from a treated pond remains in force. However, after the concentration of triclopyr TEA has decreased below 0.5 ppm a.e., treated water may used for domestic purposes. The labels and permits that govern those restrictions may be periodically changed based on new information submitted to EPA and Ecology (Table 1).

1.1.4.3 Label Restrictions

- **Label Restrictions**

  The proposed label restrictions in place as of February 2000 and the experimental labels restrictions are outlined below. However, label restrictions may change based on new data received by EPA. The current label contains the most up-to-date restrictions and the most current label should be consulted when applying a herbicide.

  Application of triclopyr TEA products must be limited to a portion of the water body at any one time because decaying vegetation can deplete the dissolved oxygen content of the water and aquatic organisms need oxygen to survive. Treatment of dense weed areas may result in dissolved oxygen decreases due to the decomposition of dead weeds. A significant decrease in dissolved oxygen content may cause the suffocation of fish or other aquatic animals. No more than one-half of a water body should be treated at one time and a waiting period of 4 to 5 weeks between treatments is required. Triclopyr TEA has a low toxicity to all species of fish and invertebrates that have been tested. The most sensitive organism is embryo/larvae of oysters, which has a 48-hour LC50 of approximately 22 ppm a.e. Since most tested species do not show chronicity when exposed to triclopyr TEA, the level of concern for this species of (0.1) may be exceeded when it is exposed at initial concentrations of 2.5 ppm a.e. However, since application to estuaries is not permitted under the triclopyr label, it is not likely that embro/larval oysters will be exposed to triclopyr TEA at concentrations high enough to cause acute or chronic impact. However, the field studies that have been conducted with triclopyr TEA to control Eurasian water milfoil, purple loose strife and waterhyacinth indicate that fish, crayfish and bivalves (freshwater clams) are not affected by triclopyr TEA when it is used at the highest recommended use rate. There have been no field studies conducted with triclopyr TEA that have shown that it is directly toxic to fish at standard maximum use rates (Petty et al, 1998; Green et al, 1989 and Gardner and Grue, 1996, Houtman, 1997, Foster, 1997). For actual size of areas recommended for treatment or other restrictions, consult the label and the permit. Note that typical control measures often do not result in the treatment of an entire water body and typically only about 20% of a water body is treated based on areas designated for priority control. Control within areas of a water body can be designated a priority based on the impact aquatic weeds may have on specific areas of the water body. These priority impacts may include recreational use, water storage and withdrawal function, flood control, irrigation, property values, human health considerations, fish and wildlife habitat, ecological health and stability, biodiversity and effects on threatened and endangered species (Getsinger in Appendix 5 of Section 1 of Endothall document).

  Most species of fish are tolerant of triclopyr TEA. The acute toxicity (LC50) of the currently used formulation (Garlon® 3A 45 to 50% a.i. = 32 to 36% a.e.) ranges from 82 ppm a.e. for rainbow trout (*Oncorhynchus mykiss*) to 182 ppm a.e. for Chinook salmon (*Oncorhynchus tshawytscha*). Formulations containing approximately 65% a.i.(46% ppm a.e.) are significantly less toxic than the current formulation. For example, the LC50 of the 65% a.i. formulation against rainbow trout is 256 ppm a.e., which is about 3-fold less toxic than the current Garlon® 3A (45% a.i.) formulation. Sensitive and environmentally relevant species such as the various salmon species (*Onchorhynchus* spp.) have demonstrated LC50s that range between 96 and 182 ppm a.e. (Wan et al, 1987). These toxicity values place triclopyr TEA in the US EPA's ecotoxicological categories of slightly toxic (LC50 = >10 to 100 ppm) to practically non-toxic (LC50 = >100 ppm). There have been no verified cases of toxicity to fish when triclopyr is used at the maximum use rate of 2.5 ppm a.e. When mortality occurs in the field after the use of triclopyr for the control of aquatic weeds, it is usually very low (≤11%) and attributable to an oxygen slump due to the presence of rapidly growing non-target aquatic plant species (Petty et al, 1998).

While formulated triclopyr (45% a.e. = 32 ppm a.e.) is not believed to be toxic to invertebrates (LC50 for embryonic/larval oysters >56 to <85 ppm formulation = >18 to <27 ppm a.e.), higher treatment rates (2.5 ppm a.e.) present a low to moderate risk to species with similar sensitivity (RQ = 0.11 = EEC/LC50 = 2.5 ppm c.e./~22 ppm a.e.). However, the RQ is less than the high level of concern (0.5). Therefore, if triclopyr TEA is treated as a restricted use herbicide, it should not cause adverse impact to the invertebrate biota. Other species of invertebrates are virtually unaffected by triclopyr TEA. For example, all other species of invertebrates that were tested have an LC50 of >100 ppm a.e. These include *Daphnia magna* (LC50 = 376 ppm a.e.), grass shrimp (LC50 = >234 ppm a.e.), pink shrimp (LC50 = 281 ppm a.e.), fiddler crab (>314 ppm a.e.) and crayfish (LC50 >103 ppm a.e.). Therefore, the observed toxicity values against these invertebrates place triclopyr TEA in the EPA's ecotoxicology categories of slightly toxic to practically non-toxic. In the field where triclopyr TEA was used to control Eurasian watermilfoil, waterhyacinth or purple loosestrife, no invertebrate mortality or changes in invertebrate population structure was seen that could be attributed to the use of triclopyr TEA (Petty et al, 1998, Green et al, 1989 and Gardner and Grue, 1996, Houtman et al, 1997, Foster et all, 1997 and Woodburn, 1988). It is unlikely that triclopyr TEA will pose an adverse impact on fish, crayfish or clams when it is applied at the maximum use rate to small treatment areas in a large water body. No residues are expected in the edible tissue of non-game and game fish. However, since triclopyr bioaccumulates at low levels (~1.0 to 2.0 in crayfish and clams), further evaluation of the accumulation effects of triclopyr on clams and crayfish should be considered before establishing residue tolerance limits on these species. The current proposed residue tolerance for fish and shellfish is 0.2 ppm a.e.

Triclopyr TEA has been reported to control invasive species of aquatic macrophyte including Eurasian watermilfoil (*Myriophyllum spicatum*), parrotfeather (*Myriophyllum aquaticum*), waterhyacinth (*Eichhornia crassipes*), alligatorweed (*Alternanthera philoxeroides*) and purple loosestrife (*Lythrum salicaria*), but does not control desirable native species like rushes (*Juncales* spp. and *Scirpus* spp.), cattails (*Typha* spp.), duckweed (*Lemna* spp.), Flatstem pondweed (*Potamogeton zosteriformis*), Coontail (*Ceratophyllum demersum*), Southern naiad *(Najas guadalupensis*), American pondweed (*Elodea canadensis* and water paspalum (*Paspalum fluitans*) and most species of algae including the green algae (*Spirogyra* spp., *Cladophora* spp., *Mougeotia* spp. *Volvox* spp., *Closterium* spp. and *Scenedesmus* spp.), *Chara* spp. and *Anabaena* spp. (Getsinger et al, 2000; Woodburn et al, 1993; Petty et al, 1998 and Green et al, 1989, Foster et al, 1997, Woodburn, 1988 and Houtman, 1997). However, southern naiad, American waterweed and coontail may be adversely impacted at higher concentrations (2.5 ppm a.e.). Even non-target aquatic plants that are typically used in testing appear to be largely unaffected by the effects of triclopyr TEA. The most sensitive species of algae and aquatic macrophytes include *Anabaena flos-aquae*, *Skeletonema costatum* and *Lemna gibba* with EC 50s of 4.2, 3.6 and 6.4 ppm a.e., respectively. Since the initial concentration is 2.5 ppm a.e., sensitive non-target aquatic species of plants and algae are not likely to be affected. Generally speaking, if the risk quotient for the most sensitive species of aquatic plant does not exceed the level of concern (1.0) the biota is considered to be protected. Since there will be a 120-day restriction on irrigation, it is unlikley that sensitive upland terrestrial species will be affected by the use of triclopyr TEA to control aquatic weeds. However, drift from treatments to control wetland associated species has the potential to damage sensitive terrestrial plants including grapes, tobacco, vegetable crops, flowers or other desirable broadleaf plants.

Since the effects of triclopyr TEA exhibit no significant chronic toxicity, the EEC should be based on the initial exposure concentration (0.75 to 2.5 ppm a.e.) and not on a time weighted average of 4 days for acute exposure or 28 days for chronic exposure. Furthermore, the half-life of triclopyr TEA in water typically ranges up to 4 days in open water and 7.5 days impounded water. Therefore, the 1 and 2-day time weighted average dosage would not be expected to vary significantly from the initial exposure concentration in still waters, which is EPA's worst case scenario.

- **Additional Restrictions Imposed by Washington State**

In the 1992 Supplemental Environmental Impact Statement for the Aquatic Plant Management Program for the State of Washington, Ecology discusses a number of additional restrictions required when triclopyr TEA is permitted for aquatic weed control. Triclopyr TEA (Renovate®) has been applied in Washington State at Loon Lake in 1998, the Okanogan River floodplain in1999, Mason Lake in 1999, Diamond Lake in 1999, Thomas Lake in 1999, Little Pend Oreille Lakes in 1999 and Liberty Lake in 1999. This product has been applied under an EPA Experimental Use Permit (Permit No 62719-EUP-1) using an Experimental label for Renovate® issued by DowElanco. The target weed was Eurasian watermilfoil for all sites except the Okanogan River floodplain where the target weed was purple loosestrife. Although the experimental label indicates that Eurasian watermilfoil may be controlled at concentrations ranging from 1.0 to 2.5 ppm a.e., the maximum use rate specified in the permit is site specific. Also the maximum area which may be treated is specified in site specific permits. Under the experimental use permits, various restrictions may be applied by the state. These restrictions may include: 1) restrictions on application rate; restrictions on area to be treated; 2) requirements for observing and reporting effects on human health, wildlife and the environment; 3) require measures to preserve or enhance wildlife; 4) additional requirements for disposal of unused herbicide; 5) requirements for collecting water for triclopyr residue analysis; 6) restrictions on applying the product when specific (*Lobelia* spp.) endangered or threatened plant species are present; 7) requirements to evaluate efficacy; 8) provisions for supplying drinking water for a time specified after the treatment of a water body that is used as a potable water supply; 9) requires measures to reduce erosion; 10) requires measures to reduce air emissions; 11) required measures to reduce noise; 12) required measures to reduce or prevent the displacement of people who reside or work in or near the area of treatment; 13) required measures to reduce the impact on recreational activities; 14) prohibit swimming for 24 hours after treatment, prohibit fishing for 30 days after treatment and digging or trapping of shellfish and crayfish for 15 days after treatment; 15) require that public notices be placed and marker buoys be placed in the treatment areas for 30 days.

Renovate® should not be applied within one contiguous mile of a potable water intake. Domestic water users must agree not to use water for at least 21 days if it is necessary to apply Renovate® within the 1-mile setback distance (State permits for years 1998 to 2000)

If legal permission can be obtained to close an outlet gate, the gate should be closed for the duration of the water use restriction specified on the experimental label. Longer periods of outlet gate closure may be specified in the permit due to local conditions or practices. Closure of the water outlet gate for up to twice the labeled water use restriction period has been recommended for products which have water use restriction similar to those of triclopyr TEA (Ecology, 1992).

When treating a water body for weed control, the applicator must use the lowest efficacious treatment rate, and 20 to 25% of the macrophytes in the water body should not be treated in order to provide refuge and habitat for aquatic animals and water fowl.

Follow all additional conditions, public notice, posting procedures and chemical restrictions contained in the permit.

1.1.3.4 Labeled Use

Triclopyr TEA products that will be labeled for use in ponds and lakes by the US EPA, include Renovate® from SEPRO Corporation and Garlon® 3A from DowElanco. Emersed plants or plants with floating leaves (waterhyacinth, alligatorweed, American lotus, waterlilies and waterprimrose) should be treated at the surface with Renovate® or Garlon® 3A at rates of 0.5 to 2 gallons formulation/acre (1.5 to 6 lbs a.e./acre) in 20 to 200 gallons of water/acre. Only the weed mass should be sprayed. Higher rates will be necessary if the plants are mature, if the weed mass is dense or if a difficult to control species is present.

Annual and perennial herbaceous weeds (bindweed, burdock, Canada thistle, chickory, curly dock, lambquarter, plantago, purple loosestrife, ragweed, tansy ragwort, vetch and wild lettuce) should be treated at rates of 0.33 to 2 gallons formulation/acre (1.0 to 6 lbs a.e./ha) in 20 to 100 gallons/acre. Weeds should be treated when they are young and actively growing before the bud or early bloom stage.

Woody brush and patches of perennial herbaceous weeds should be treated at 2 to 3 gallons/acre (6 to 9 lbs a.e./acre) in 20 to 100 gallons of water/acre. The foliage should be thoroughly wetted with the spray solution.

For the control of submersed weeds (Eurasian watermilfoil, parrotfeather or pennywort), Renovate® should be applied at concentrations of 1.0 to 2.5 ppm. The herbicide may be applied as a surface or subsurface application. For best results, weeds should be treated when they are actively growing.

Surfactants are not necessary when using triclopyr products to control submersed vegetation. However, when triclopyr products are used to control floating or emerged weeds, a non-ionic surfactant at the labeled use rate should be combined with the diluted liquid formulation to assist with sticking and penetration of the pesticide. This has the effect of reducing both the application rate and the cost of the application. Care should be taken to select a surfactant that has been approved for aquatic use. Surfactants approved for aquatic use will not harm fish. Thickening agents like PolyControl® or one of the organosilicates are often added to herbicide solutions that are applied to the water surface in order to control drift (Kurt Getsinger, Army Corp of Engineers interview, Appendix 5 of Endothall Section 1 document).

When liquid formulations of triclopyr TEA are applied by subsurface injection, the use of surfactants is not necessary. However, thickening agents may be used to allow the liquid triclopyr TEA product to drop lower in the water column where it will be more effective (Kurt Getsinger, Army Corp of Engineers interview, Appendix 5 of Endothall Section 1 document).

1.1.3.5 Effectiveness Controlling Specific Aquatic Plant Species

In the control of aquatic weeds, triclopyr TEA is a broad-spectrum systemic herbicide. The mode of action against macrophytes is similar to 2,4-D and triclopyr TEA appears to function as an auxin mimic which causes epinastic growth in the meristem of the treated plant. However, the exact reason for the death of treated plants is not entirely understood. Triclopyr TEA is effective against a wide variety of aquatic and wetland associated weeds (Table 2) at application rates of 0.33 to 3 gallons of formulation per surface acre. For the control of aquatic plants, the concentration in the water column should be 0.75 to 2.5 ppm a.e. According to the labels, Renovate® and Garlon® 3A typically control a large number of aquatic weeds and wetland associated annual and perennial herbaceous weeds. These products are also effective against many species of woody brush plants. The primary species controlled are Eurasian watermilfoil (*Myriophyllum spicatum*), waterhyacinth (*Eicchornia crassipes*), and purple loosestrife (*Lythrum salicaria*). Other species that are controlled may be found in Table 2 and the woody brush species that are controlled are listed in the Garlon® 3A label. For rates of applications to control these species, consult the proposed Garlon® 3A label (2000). Triclopyr TEA products are not effective against algae (blue-green, green, diatoms and probably rooted macrophytic algae like *Chara* spp.), and duckweed (*Lemna* spp.). Also, most native species of aquatic macrophytes, including coontail (*Ceratophyllum demersum*), Southern naiad *(Najas guadalupensis*), American waterweed (*Elodea canadensis*), rushes (*Scirpus* spp.), cattails *(Typha* spp.) and flatstem pondweed (*Potamogeton zosteriformis*) are not controlled by triclopyr TEA. However, some of these species (particularly coontail, southern naiad and American waterweed) may be adversely impacted by higher treatment rates (2.5 ppm a.e.).

Garlon® 3A and Renovate® may also incidentally control species of aquatic and wetland associated weeds for which no efficacy is claimed. However, these products should not be used to control species or groups of weeds not mentioned in the label. Since the Renovate® experimental label does not specify many of the species that triclopyr TEA controls, it is recommended that expert advice be sought for control of species not specified in the label before control is attempted on species that the label does not particularly specify.

Certain species of aquatic macrophytes are of particular interest to Ecology. They are *Myriophyllum spicatum* (Eurasian watermilfoil), *Lythrum salicaria*, (purple loosestrife), *Egeria densa* (Brazilian elodea), *Myriophyllum aquaticum* (parrotsfeather), *Cabomba* *caroliniana* (fanwort), *Hydrilla vertcillata* (hydrilla), *Tamarix ramosissima* (saltcedar), *Amorpha fruticosa* (indigobush), *Polygonum sachalinense*, (giant hogweed or giant knotweed), *Polygonum cuspidatum* (Japanese knotweed), *Lysimachia vulgaris* (garden loosestrife) and *Phalaris arundinacea* (reed canarygrass).

Garlon® 3A and Renovate® claim efficacy against a number of these weeds of special concern including Eurasian watermilfoil, parrotsfeather and purple loosestrife. Some concern has been expressed about the general efficacy of triclopyr for the control of aquatic weeds. Langeland and Smith (1993) recommend a mixture of triclopyr TEA and diquat alone or in combination with various surfactants to broaden the spectrum of control. Triclopyr TEA plus diquat at 0.83 ppm a.e. triclopyr TEA and 0.28 ppm c.e. diquat was effective in controlling water hyacinth and waterlettuce.

Some species of aquatic plants are known to resist or tolerate triclopyr TEA. These species are rushes (*Scirpus* spp.), cattails (*Typha* spp.), coontail (*Ceratophyllum demersum*). Duckweed (*Lemna* spp.) and flatleaf pondweed (*Potamogeton zosterifomis*). When the biomass of other aquatic species is decreased by triclopyr TEA use, tolerant species have the potential to become dominant and decrease plant diversity in the treated area. However, the elimination of monoculture stands of Eurasian watermilfoil or purple loosestrife may improve wildlife and salmon habitat by allowing a greater diversity of native plants to replace these noxious species.

Use of triclopyr TEA products (Garlon® 3A or Renovate®) to control weeds not listed on the label is not recommended. However, these weeds may be controlled incidentally as a result of application of triclopyr products for the control of species listed on the label.

1.1.3.6 Other Concerns

Although it is not the practice of Ecology to permit the use of tank mixes, triclopyr tank mixes with other herbicides have the potential control a broader spectrum of weeds than is possible with ticlopyr alone. For example, triclopyr and diquat have been proposed to be used as a tank mix to control waterhyacinth and waterlettuce. Failure to control these species in Lake Okeechobee (Florida) has resulted in the destruction of hundreds of acres of native plant communities which are important nesting habitat for the endangered Snail Kite (*Rostrhamus sociabilis*) (Langeland and Smith, 1993). Concerns for effects on endangered, threatened or desirable native plant species may also impact when triclopyr TEA is use to control aquatic and wetland weeds. Removal of Eurasian watermilfoil or purple loosestrife may improve habitat for growth and reproduction of many native plant species. Other native plant species like coontail, southern naiad, American waterweed or *Lobelia* spp. may be adversely impacted by use of the higher labeled rates of triclopyr TEA.

Various non-ionic surfactants have been used with triclopyr for the control of floating and emergent aquatic vegetation. One of the main purposes in using a surfactant is to decrease the amount of active ingredient necessary to control floating and emergent aquatic vegetation. Some common surfactants used with aquatic herbicides are X-77®, CideKick®, PolyControl® and SunWet®. Non-Ionic aquatic surfactants registered for use with aquatic herbicides like triclopyr TEA should not be toxic to fish or aquatic invertebrates.

The rate of herbicide use is controlled by a number of use pattern factors. These factors may include the species of plant to be controlled, the degree of infestation, the contact time between the treated water and the plants to be controlled, usage patterns including susceptibility of the treated plant species, depth of the water, temperature of the water and water exchange patterns. Presence of a dense weed population may require a higher use rate to achieve control than a sparse weed population. Concentration X exposure time is usually proportional; that is, a low concentration requires a longer exposure time to achieve control than a high concentration. Water, which has a high flow rate, large volume dilutions from ground water or surface water sources or extensive vertical and lateral mixing, may require higher use rates than still or impounded water, which has little dilution or mixing.

1.1.4 Maintaining the Current Registration

Since the last Supplemental Environmental Impact Statement (1992), a number of additional studies compliant with the EPA's FIFRA Pesticide Assessment Guidelines and Good Laboratory Practice Standards have been completed and submitted to the US EPA for review. Studies that are compliant with current regulations not only add to the database but also increase the confidence of regulatory organizations, elected officials and the general public that the data supports the most recent risk assessment (EPA RED, 1998). However, it is of some concern that the values reported in the EPA RED (1998) often do not agree with the values reported in the original documents. In the EPA RED (1998) LC50/EC50 values are reported as being ppm a.i.; but examinations of the original documents indicate that these values are often reported in ppm as received (formulation equivalence). Therefore, the LC50/EC50 values reported in EPA RED are often 2-fold higher on an a.i. basis than the original documents indicated. These studies will result in the addition of an aquatic use for triclopyr TEA and an expansion of the irrigation restriction from 21 to 120 days and a change of the set back distance for potable water intakes from 1 mile to a maximum of 2,000 feet with the absolute distance based on the size of the treatment area. The changes brought by the development of new data will be assessed in later sections of this document.

1.1.5 Interviews with Applicators regarding Typical Practices in Washington State

A set of questions was developed based on specific points of interest outlined by Ecology. The items that were addressed were those that the applicators (Doug Dorling of Allied Aquatics, Inc. and Terry McNabb of Resource Management, Inc.) would have direct knowledge of. Their input was incorporated in the main body of Section 1. The original questions and answers given by the applicators are presented in Appendices 3 & 4 of Section 1 for endothall. Prior to finalization of the interviews, the respondents were requested to review the documents, correct any errors and elaborate on points of particular interest or concern to them.

1.1.6 Rate Technologies

The same set of applicator questions was also asked of Kurt Getsinger of the Army Corp of Engineers. Dr. Getsinger heads the Chemical Technologies Research Unit at Waterways Experiment Station. Dr. Getsinger is a leading expert and scientist in chemical control technologies. He is the author of many scientific papers in this field and co-author with Howard Westerdahl of the "Aquatic Plant Identification and Herbicide Use Guide" (1988). Dr. Getsinger was also asked to discuss his research in rate reduction technology including hardware, products and methods used. Dr. Getsinger's input was incorporated in the main body of Section 1 and in the assessments and recommendations portions of this document (Section 4). The original questions and answers given by Dr. Getsinger are presented in Appendix 5 of Section 1 for endothall. Prior to finalization of the interview, the respondent was requested to review the document, correct any errors and elaborate on points of particular interest or concern to him.

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LIST OF TABLES

Table 1: Rate of Application, Effective Concentrations, Comments and Label Restrictions for Garlon® 3A Specialty Herbicide and Renovate® Specialty Herbicide (Triclopyr TEA 44.4% a.i.) (31.8%% a.e.).

Comments & Label Restrictions for Garlon® 3A Specialty Herbicide and Renovate® Specialty Herbicide
Garlon® 3A or Renovate® Specialty Herbicides may be used to control certain submerged floating and emerged plant species including woody plants in ponds, lakes, reservoirs and marshes including adjacent banks and shores; it may also be used in non-irrigation ditches or canals which have little or no continuous outflow. Garlon® 3A or Renovate® may be used for control of certain woody plants and broadleaf weeds in wetlands. Wetlands include floodplains, deltas, marshes, swamps, bogs and transitional areas between upland and lowland sites. Wetlands may occur within forests, non-crop sites, wildlife habitat restoration and management areas and similar sites. Also included are areas adjacent to or surrounding domestic water supply reservoirs, lakes and ponds. For instructions on application rates to control specific weeds, see the Proposed Garlon® 3A Specialty Herbicide label (2000) and the Renovate® Specialty Herbicide Experimental Label. For the control of aquatic weeds, application rates are 0.75 to 2.5 ppm a.e. are recommended. Rates vary depending on the target species and treatment conditions. For emergent or floating weeds, the rate of application should be 0.5 to 2 gallons formulation/acre (1.5 to 6 lbs a.e./acre). The rate of application will vary depending on the species to be controlled and the density of the weed mass. A nonionic surfactant should be added to the spray mixture in quantities specified on the surfactant label. For control of broadleaf weeds and woody plants in wetland sites, 0.25 to 3 gallons formulation/acre (0.75 to 9 lbs/acre) should be applied in enough water to give uniform and complete coverage of the plants to be controlled. Use of a non-ionic surfactant is recommended for foliar applications. The specific restricted water use periods for potable purposes (drinking and livestock water) is specified as 14 days in the experimental use permit. In the proposed label is a maximum setback distance of 2,000 feet from a potable water intake (drinking). The absolute distance of this setback distance varies with the size of the treatment area. There is no specific livestock setback distance in the proposed label. However, contact with representatives of DowElanco indicates that they intended the meaning of potable water setback distance to cover livestock watering restrictions as well as domestic purpose restrictions. The irrigation restriction is 120 days or until the levels of triclopyr are lower than the limit of detection. The proposed residue levels in potable water is 0.5 ppm a.e. If concentrations in treated water are not higher than 0.5 ppm a.e., the water may be used for domestic purposes and for watering livestock. There is no fishing or swimming restriction specified in the proposed label. However, the experimental label indicates that swimming should not be allowed for 24 hours after application. Fishing should not be allowed for 30 days after application according to the experimental use label. The harvesting of shellfish (bivalves and crayfish) should not be allowed for 15 days after application. Garlon® 3A and Renovate® are particularly effective against *Myriophyllum spic*atum, *Eichhornia crassipes* and purple loosestrife (*Lythrum salicaria*). However, triclopyr TEA products also control other species listed in Table 2 and woody brush species listed in the Renovate® label. For best control triclopyr TEA should be applied when the plants are young and actively growing and before buds or flowers are present.

Species that are not effectively controlled with triclopyr TEA include rushes (*Scirpus* spp.) cattails (*Typha* spp.), coontail (*Ceratphyllum demersum*) duckweed (*Lemna* spp.), pondweed (*Potamogeton* spp.), American waterweed (*Elodea canaden*sis), southern naiad (*Najas guadalupenis*), and water paspalum (*Paspalum fluitans*) Triclopyr TEA is also ineffective in the control of algal species.

A nonionic surfactant may be applied at rates recommended on the surfactant label for the control of floating, emergent or wetland associated terrestrial plants. Thickening agents may be added to the spray mixture to control drift in surface applications and allow subsurface applications to sink lower into the water column where they will be more effective.

To minimize the effects of triclopyr on aquatic animals, it should not be applied to more than half of the water body at one time and four to five weeks should be allowed before the other half of the water body is treated. The purpose of this restriction is to prevent suffocation of fish due to a decrease in the dissolved oxygen content that typically occurs due to the decay of dead and moribund vegetation. Also, treatments of water bodies should occur from the edge of a water body outward toward the center. This allows for escape of fish from the area being treated prior to its treatment. Since triclopyr TEA is new to the aquatic market, there is little data available on the effects of triclopyr treatment on water quality. However, data from Lake Seminole in Georgia and Lake Minnetonka in Minnesota as well as ponds in California, Missouri and Texas indicates that no changes in water quality occur due to the proper use of triclopyr TEA to control aquatic weeds.

Table 2: Species Controlled, Effectiveness of Control and Registration Status for Listed Species

Species Controlled	**Labeled Use and/or Effectiveness of Control**
	Garlon® 3A or Renovate® 44.4% Triclopyr DEA (31.8% Triclopyr acid equivalence)
Alternanthera philoxeroides[1] (Alligatorweed)	Labeled Use. Only partially controlled (top growth) if plants are growing in water.
Nelumbo lutea[1] (American lotus)	Labeled use
Convolvulus spp.[2] Bindweed	Labeled use
Arctium minus[2] (Burdock)	Labeled use
Circium arvense[2] (Canada thistle)	Labeled use
(Chickory)[2]	Labeled use
Rumex crispus[2] (Curly dock)	Labeled use
Taraxacum officinale[2] (Dandelion)	Labeled use
Myriophyllum spicatum[3] (Eurasian watermilfoil)	Control achieved at 0.75 to 2.5 ppm a.e. Higher rates required in areas of greater water exchange. Areas of greater water exchange may require repeat applications.
Convolvulus arvensis[2] (Field bindweed)	Labeled use
Hypochaeris radicata[2] (Frogbit)	Labeled use
Chenopodium album[2] (Lambsquarter)	Labeled uses
Myriophyllum aquaticum[3] (Parrotfeather)	Control achieved at 0.75 to 2.5 ppm a.e. Higher rates required in areas of greater water exchange. Areas of greater water exchange may require repeat applications.

Species Controlled	**Labeled Use and/or Effectiveness of Control**
	Garlon® 3A or Renovate® 44.4% Triclopyr DEA (31.8% Triclopyr acid equivalence)
Hydrocotyle spp.[3] (Pennywort)	Control achieved at 0.75 to 2.5 ppm a.e. Higher rates required in areas of greater water exchange. Areas of greater water exchange may require repeat applications.
Plantago spp.[2] (Plantain or Indian wheat)	Labeled use
Lythrum salicaria[2] Purple loosestrife	Labeled use
Ambrosia spp.[2] Ragweed	Labeled use
Senecio jacobea[2] (Tansy ragwort)	Labeled use
Solanum aculeastum[2] (Tropical sodaapple)	Labeled use
Vicia spp.[2] (Vetch)	Labeled use
Eichhornia crassipes[4] (Waterhyacinth)	Repeat treatments may be necessary to control re-growth of plants missed in previous treatment.
Nypmphaea odorata[1] (Waterlilily)	Labeled use
Nuphar spp.[1] (Waterlily)	Labeled use
Ludwigia uruguayensis[1] Waterprimrose	Labeled use
Lactuca spp.[2] Wild lettuce	Labeled use

1 Emersed plant.
2 Wetland associated terrestrial plant.
3 Submersed plant.
4 Floating plant.

LIST OF APPENDICES

Appendix 1: Experimental Renovate® Label

Please go to the following web site for the newest information

http://www.sepro.com/pdf_lit/aquatics/Renovate_Label.pdf

Appendix 2: Garlon® 3A Proposed Label

Please go to the following web site for the newest information

http://www.cwc-chemical.com/downloads/DowAgrosciencesDownloads/Garlon3ALabel.pdf

Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides

Triclopyr

Volume 5, Section 2

CHEMICAL CHARACTERISTICS

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2.0 CHEMICAL CHARACTERISTICS

The physical/chemical data in the following section are those required by USEPA when a product is registered for use in the US as a pesticide. These characteristics assist in the basic understanding of the molecule and are later used in predicting environmental behavior or are considered when higher tiered studies are designed or requested. Pure active ingredient or technical grade active ingredient (TGAI) refers to the active compound(s), which cause the desired biological effect when applied to a target system. Manufacturing Use Products (MUP) are the TGAI with additional added ingredients. Typically, the added ingredients are solvents or safeners. The technical grade active ingredient is typically formulated into end-use products, also known as formulated products. The end-use products consist of a known percentage active ingredient plus a solvent or solid carrier and may include surface active components to aid in dissolution, emulsification, suspension, *etc.*, of the active ingredient.

2.1 TRICLOPYR

Triclopyr, ((3,5,6-tricholoro-2-pyridinyl)oxy)acetic acid is the active component in aquatic herbicides used in static and flowing water to control aquatic weeds. It is also registered for a number of terrestrial uses including broadleaf weed control and is used in rice, pasture and rangeland, rights-of-way, forestry and turf, including home lawns and gardens. Triclopyr is a non-selective contact herbicide of the auxin type. These herbicides are capable of moving from leaves (sources of sugar production) with sugars to sites of metabolic activity (sinks of sugar utilization) such as underground meristems (root tips), shoot meristems (shoot tips), storage organs and other live tissues. Since movement to sites is essential for continued plant growth, these herbicides have the potential to kill simple perennial and creeping perennial weeds with only one or two foliar applications. The effects associated with auxins help set them apart from other downwardly mobile herbicides. Bending and twisting of leaves and stems is evident almost immediately after application. Delayed symptom development includes root formation on dicot stems; misshapened leaves, stems, and flowers; and abnormal roots. (EPA, 1998)(Purdue, 2000)

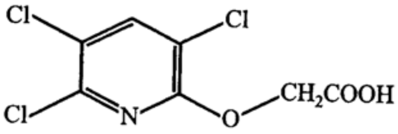
Triclopyr is formulated as a solution in water. The primary concentrated end-use product is Renovate® Aquatic Herbicide (EPA Reg. No. Not issued at this time). Renovate® may be used to control a number of submerged species as well as several species of floating and emergent weeds.

2.1.1 Composition

Triclopyr is a pyridinyloxyacetic acid. In its pure form it is a white solid with the following characteristics:

- **Active Ingredient**

Common name: Triclopyr
CAS Registry No.: 55335-06-3
Chemical name: 3,5,6-trichloro-2-pyridinyloxyacetic acid
Empirical formula: $C_7H_4Cl_3NO_3$
Molecular weight: 256.5
Structure:



- **Impurities**

There are no known impurities identified by the manufacturers or the US EPA which are known to be of toxicological or environmental concern. The US EPA has established guidelines that require that impurities of concern, such as N-nitrosoamines, ethylenedibromide and chlorinated dioxins and furans must be disclosed. No such compounds are present in triclopry products.

The primary intentionally added inert or "other" ingredient in triclopyr formulations is water. In addition, triethanol amine is used to form the salt of triclopyr, imparting water solubility to the active ingredient for the formulation process. Other formulation ingredients, when included in the end-use products, have been reviewed by the USEPA and approved when used for their intended purpose, however, these are not reported, as they are confidential manufacturing information.

The USEPA has established a category listing system for the "other" (inert) compounds used in pesticide formulations. The lists are designated 1, 2, 3, 4a and 4b. Compounds are assigned to the various lists according to their toxicological concern and to the extent their safety has been reviewed by the Agency. In the case of each list, if USEPA determines that a compound is no longer used in any pesticide formulation, it will be removed from the list.

List 1 contains eight compounds, which, due to their toxicological profile, require special labeling if used in a pesticide formulation. These compounds are generally not used in pesticidal formulations any longer. There are no List 1 compounds in the triclopyr formulations used in the State of Washington.

List 2 compounds are those for which USEPA has not yet determined a full profile but is reviewing existing information. At the completion of their evaluation, it is expected that the compounds still in use in pesticide formulations will be moved to List 1 or to List 4. There is one List 2 compound in the triclopyr formulations used in the State of Washington (triethanolamine).

List 3 contains those compounds which have not been fully evaluated, but which have profiles of lesser concern in the USEPA evaluation scheme. It is expected that most of these compounds will be moved to List 4 once their evaluation by the Agency is complete. There are no List 3 inert compounds in the triclopyr product registered for use in the State of Washington.

List 4 is divided into two categories. List 4A contains compounds generally regarded as safe for use in pesticide formulations and includes such compounds as corn cobs and attapulgite clay. List 4B contains those compounds that have sufficient data on file at EPA to substantiate that they can be used safely in pesticide products.
In addition to the above-mentioned review by the USEPA, all registered pesticidal end-use products (the products actually applied to the environment to control weeds

or pests) must undergo a series of toxicological tests to establish their safety. Because these tests are performed on the actual end-use formulation, the effects of the "other" ingredients are effectively tested simultaneously. This toxicological screen of the "other" compounds affords an additional opportunity to examine comparative data on the active ingredient versus the end-use product to determine if there is a need to test each of them in a complete testing battery.

- **Intentionally added inert ingredients**

  Intentionally added inert or "other" ingredients in triclopyr formulations include: water and triethanol amine in the Renovate® Aquatic Herbicide formulation. The water serves as the primary diluent/solvent in the liquid product while the triethanol amine is used to form the salt of the technical grade active ingredient.

2.1.2 Color

Color is an end-point observation of the product used to assist in identification.

	Color	**Citation**
Triclopyr Technical	White	(EPA, 1995)
Renovate® Aquatic Herbicide	Peachy Amber	(Hall, 1999)

2.1.3 Physical State

Physical state is an end-point observation of the product, solid, liquid or gaseous used to assist in identification.

	Physical State	**Citation**
Triclopyr Technical	Solid	(EPA, 1995)
Renovate® Aquatic Herbicide	Liquid	(SePRO, 2000)

2.1.4 Odor

Odor is an end-point observation of the product used to assist in identification. Odor may also serve as a warning in cases where odorants are added as a safety factor.

	Odor	**Citation**
Triclopyr Technical	Earthy	(Hart, 1987)
Renovate® Aquatic Herbicide	Characteristic Amine	(Hall, 1999)

1.1

2.1.5 Melting Point

The melting point is a physical end point observation used for identification of pure compounds and may provide some indication of thermal stability. Melting point is not applicable to the formulations because they are liquids.

	M.P. (°C)	Citation
Triclopyr Technical	~148-150°	(EPA, 1995)

2.1.6 Boiling Point

The boiling point is a physical end point observation for identification of pure compounds. The boiling point for the pure acid active ingredient is not applicable as it is a solid. The boiling points for the liquid formulation is essentially the same as water, 100°C as it is aqueous based.

2.1.7 Density, Bulk Density or Specific Gravity

Bulk density is a measure of the weight per unit volume of the product and is useful for physical identification or differentiation of two similar products. The value may also be needed to calculate application rates in some instances. Density is typically reported as grams per cubic centimeter at 25°C.

	Density (g/cc)	Citation
Triclopyr Technical	1.26	(Hart, 1987)
Renovate® Aquatic Herbicide	1.079	(Hall, 1999)

2.1.8 Solubility

Solubility is a physical end point useful for understanding potential environmental impact. High water solubility is frequently associated with mobility and affects distribution in water and soil. This endpoint is determined for the active ingredient in a product and is typically reported as grams per 100 ml water at 25°C.

	Solubility in Water @ 25°C (g/100 ml)	Citation
Triclopyr Technical	>70.0	(SePRO, 2000)
Renovate® Aquatic Herbicide	Miscible with Water	(SePRO, 2000)

2.1.9 Vapor Pressure

Vapor pressure is a physical end point useful for understanding the distribution of the active ingredient between water/soil and air. High volatility is an indication of potential impact in the air compartment. This endpoint is determined for the active ingredient in a product and is typically reported as mm mercury (Hg) at a specified temperature.

	Vapor Pressure @ 24.3°C (mm Hg)	**Citation**
Triclopyr Technical	1.26×10^{-6}	(SePRO, 2000)
Renovate® Aquatic Herbicide	N/A	N/A

1.2

2.1.10 Disassociation Constant

Disassociation constant is a physical end point used to assess the distribution of the product in aqueous media. The acid is generally fully dissociated at pH's greater than 5. The amine salt in the end-use product is dissociated rapidly in water making the anion the predominant species in most natural waters. (EPA, 1995)

	Dissociation Constant (pK_a)	**Citation**
Triclopyr Technical	2.93	(EPA, 1998)
Renovate® Aquatic Herbicide	2.93	(EPA, 1998)

2.1.11 Octanol/Water Partition Coefficient

Octanol/Water partition coefficient is a physical end point used to assess the potential of a compound to bioaccumulate in the environment. The value represents the ratio of product in octanol versus water at equilibrium at 25°C. Values less than 10 indicate little or no likelihood of bioaccumulation. This data is not required for polar organic molecules such as triclopyr.

	Octanol/Water Coefficient (Kow)	**Citation**
Triclopyr Technical	N/A	N/A
Renovate® Aquatic Herbicide	N/A	N/A

2.1.12 pH

pH is a physical end point used to identify the product and to assess the potential effect of the equilibrium in the environment. For triclopyr Technical, the value is reported for the undiluted product at 21°C. For Renovate Aquatic Herbicide, the value is reported as a 10.1 % dilution in distilled water.

	pH	Citation
Triclopyr Technical	9.54	(Hall, 1999)
Renovate® Aquatic Herbicide	9.54	(Hall, 1999)

2.1.13 Stability

Stability is a chemical evaluation of the product to assess the potential effect of heat, light, metals and metal ions on the active ingredient. In the case of triclopyr there may be significant corrosion of metals including iron, aluminum and zinc. Additional discussion of compatibility may be found in section 2.1.20, Corrosion Characteristics below. (Hall, 1999).

2.1.14 Oxidizing or Reducing Action

Oxidizing or reducing action is an assessment of the potential for a compound to react with common oxidizers or reducers. Triclopyr is not reactive monoammonium phosphate, zinc and potassium permanganate. (Hall, 1999)

2.1.15 Flammability

Determination of flammability is measurement of the temperature that will sustain a flame and is used to classify the product for hazard in storage and shipping. Determination of flammability is not required for technical grade products. The flash point of the formulated product is 43°C (110°F). (Hall, 1999)

2.1.16 Explodability

Determination of explodability is measurement of the potential for a compound to explode when exposed to physical or thermal shock. Determination of explodability is not required for technical grade products. The formulated product is insensitve to impact. It exhibits an isotherm of 564 J/g (joules/gram) at 248°C. (Hall, 1999)

2.1.17 Storage Stability

Storage stability is the physical determination of the stability of the active ingredient when stored in its commercial packaging over extended time periods, usually one to two years or more. Triclopyr has been shown to be stable for at least one year when stored in polyethylene at ambient warehouse conditions. (Hall, 1999).

2.1.18 Viscosity

Viscosity is a physical end-point measurement used to identify the product and to assess the ability of the product to be poured or pumped. The measurement is not required on technical grade products or on solid products. The viscosity is reported in milli Pascals m Pas at 25.1°C.

	$mN\ m^{-1}$	Citation
Triclopyr Technical	N/A	N/A
Renovate® Aquatic Herbicide	12.1	(Hall, 1999)

2.1.19 Miscibility

Miscibility is a physical assessment of the ability of a formulated product to mix with spray oils for use during application. Since the triclopyr aquatics products are not labeled for application in oil, this data requirement is not applicable.

2.1.20 Corrosion Characteristics

Corrosion characteristics requires the physical observation/measurement of the effects of the product on the commercial packaging. Measurements of the weight, deformation and strength of the packaging are reported. For triclopyr there is no significant corrosion of commercial packaging including flourinated High Density Polyethylene, resin lined steel and stainless steel. (Hall, 1999)

2.1.21 Dielectric Breakdown Voltage

Dielectric breakdown voltage is the physical measurement of the effect of an electric arc on the stability of the formulated product. This requirement applies only to formulations that are applied around electrical equipment or apparatus. As there is no likelihood of open electrical apparatus in the aquatic environment, this test is not applicable.

REFERENCES

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Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides

TRICLOPYR

Volume 5, Section 3

ENVIRONMENTAL FATE

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3.0 TRICLOPYR

Triclopyr has been used as an herbicide for a number of years in both terrestrial and aquatic weed control. Due to its high profile and proposed registered use as an aquatic herbicide, there have been a number of relatively recent studies conducted to support the registration of Garlon® 3A and Renovate® for control of aquatic (submerged and emerged) and wetland weeds. The active ingredient in Garlon® 3A and Renovate® is triclopyr triethylamine salt (44.4% triclopyr TEA; 31.6% triclopyr acid equivalence = 3 lbs a.e./gallon. Triclopyr TEA is a new product for the control of aquatic weeds, therefore, it is not mentioned in Ecology's Environmental Impact Statement (EIS) issued in 1993. This report contains citations from review articles and original publications published to determine the fate and behavior of triclopyr TEA in aquatic environments. In addition, several "registration" studies performed by registrants for EPA are cited (EPA RED, 1998).

The Washington State Department of Ecology is considering triclopyr TEA for use only in aquatic weed management. While a large amount of information is available on the environmental fate of triclopyr butoxyethyl ester (triclopyr TEA) and triclopyr acid (herbicides structurally similar to triclopyr TEA), less information was located on Triclopyr TEA in the literature. When data for triclopyr TEA and triclopyr acid are cited, the citation is meant to augment or expand information on triclopyr TEA. The work of greatest value has been conducted on triclopyr TEA or triclopyr acid, which are known to degrade in a similar manner and rate, and are believed to be of similar toxicity to most aquatic animals and wildlife. Triclopyr acid, is the active substance in triclopyr TEA and triclopyr BEE. Attention should be paid to the differences in hydrolysis, photolysis, and other results in this section, and data generated from sources of triclopyr other than triclopyr TEA and triclopyr acid should be interpolated with caution when predicting triclopyr behavior in the environment. For example, triclopyr BEE generates different photolysis products than triclopyr TEA and triclopyr acid. Furthermore, triclopyr BEE should be less mobile than triclopyr TEA or triclopyr acid particularly at lower pHs. Triclopyr BEE forms triclopyr acid and 2-hyroxybutanol (BEOH) rapidly at basic pHs. After the formation of triclopyr acid from triclopyr BEE, the rate of degradation and degradates produced will be similar to those seen with triclopyr TEA.

3.1 VOLATILIZATION

Limited data were found regarding triclopyr volatilization. The following information was obtained from the 9th edition of the Pesticide Manual (Worthing and Hance et al, 1991) and the EPA (EPA RED, 1998).

Available data indicate that the vapor pressure of triclopyr acid is very low. At 25°C, the vapor pressure of triclopyr acid is 1.26×10^{-6}mmHg and has a solubility of 430 ppm a.e. Triclopyr TEA is a non-volatile, very soluble salt of triclopyr acid with a vapor pressure of $<1\times10^{-8}$ mmHg and a solubility of 4.12×10^{5} ppm at pH 7. Triclopyr BEE is a nonvolatile ester of triclopyr acid with a vapor pressure of 3.6×10^{-6} mmHg and a solubility of 6.8 ppm (EPA RED, 1998). The Henry's Law constant for triclopyr acid, triclopyr TEA and triclopyr BEE was calculated by the EPA (EPA RED, 1998) to be 9.65×10^{-10}, $<1.15\times10^{-14}$ and 2.47×10^{-7} atm•meter^{3}/mole, respectively. This is somewhat misleading since triclopyr is not believed to partition significantly from water to air.

Triclopyr TEA will not persist as the salt under normal environmental conditions. In measurements of conductance of a solution of triclopyr TEA in water as a function of time, triclopyr TEA dissolved and dissociated completely to TEA acid within one minute. Therefore, the Henry's constant value for triclopyr TEA is essentially equivalent to the Henry's constant value for triclopyr acid. Also, triclopyr BEE hydrolyzed quickly to triclopyr acid in natural waters, with a half-life of 0.5 days at pH 6.7. Supplemental information indicates that triclopyr BEE degrades to triclopyr acid with a half-life of ~3 hours when applied to silty clay, silt loam and sandy loam soils. In all three soils, less than 3.2% of the applied triclopyr BEE remained after 48 hours. This behavior was also observed in the field. The half-life of triclopyr BEE in a terrestrial field dissipation study was 1.1 days, while the total triclopyr (Triclopyr BEE plus triclopyr acid) half-life was 10.6 days. Therefore, the Henry's constant for triclopyr BEE is essentially equivalent to the Henry's constant for triclopyr acid. Given these characteristics, the volatilization half-life for triclopyr acid, triclopyr TEA and triclopyr BEE are essentially infinite in an aquatic system at 25°C and 1-meter depth. Therefore, triclopyr in any of its formulations can be considered non-volatile (Wauchope et al, 1992).

Although the volatility of triclopyr is low, there is an aerial application restriction in Arkansas of one-quarter mile from susceptible crops when it is used to control broadleaf weeds in rice (Johnson et al, 1995). The low volatility makes it unlikely that triclopyr will adversely impact applicators. The highest exposure level to applicators due to inhalation is not more the 35 μg per 8-hour day when triclopyr TEA (Garlon® 3A) is applied at typical rates (0.84 a.e./hectare) along highway right-of-ways in Louisiana (Abdelghani, 1995).

No additional studies were found regarding the volatility or water solubility of triclopyr acid triclopyr TEA or triclopyr BEE.

3.2 HYDROLYSIS

Summary: *Triclopyr acid did not hydrolyze significantly in sterile buffered water. The hydrolysis half-life cannot be measured since degradation of triclopyr acid was reported as being insignificant. Therefore, the hydrolysis half-life can be presumed to be greater than 30 days, and probably greater than one year, in sterile buffered water at pHs 5, 7 and 9. Since triclopyr TEA dissociates to the conjugate base (free acid) of triclopyr acid in less than one minute in water, triclopyr TEA will also be stable to hydrolysis. Triclopyr BEE is transformed to the conjugate base of triclopyr acid. At a temperature of 25°C, triclopyr BEE is hydrolyzed to triclopyr plus 2-hyroxybutanol (BEOH) with a half-life 84 days at pH 5, 8.7 days at pH 7 and 0.3 days at pH 9 in sterile buffered water. In natural water with a pH of 6.8, triclopyr BEE is hydrolyzed to triclopyr acid plus BEE in ~0.5 days. This transformation of triclopyr BEE to triclopyr acid plus BEE is temperature sensitive and in general follows the Q10 principle where for every 10°C increase in temperature, the rate of hydrolysis increases by two- to three-fold. The rate of this transformation is impacted by buffer catalysis effects with the rate of transformation increasing as the buffer concentration increases; that is the half-life decreases as the buffer concentration increases. Therefore, this transformation may be faster in the laboratory than in the natural environment because of high buffer strength and elevated temperatures (EPA RED, 1998, Szeto, 1993 and McCall et al, 1988). Since the pH of most natural water ranges from 6 to 9, with higher values during higher bio-productivity in summer, triclopyr acid and triclopyr TEA will not be hydrolyzed when used in rivers, canals, reservoirs, lakes and ponds. Therefore, although triclopyr BEE*

would be rapidly hydrolyzed to triclopyr acid plus BEOH, the remaining triclopyr acid should be stable to the effects of hydrolysis.

Hydrolysis refers to the chemical interaction of the chemical with water as a mechanism of chemical breakdown. While aqueous or aquatic (the terms are synonymous in this review) persistence studies are sometimes conducted in natural water bodies, true hydrolysis studies are conducted in laboratories using sterile distilled or deionized buffered water so that the chemical effects of an aqueous environment can be isolated from biological, sunlight, or sediment interactions. Aquatic persistence in natural water is addressed in Section 3.5.

Laboratory hydrolysis studies for EPA submission are typically performed with radioactive ^{14}C-triclopyr at three pH values (pH 5, pH 7, pH 9) corresponding to slightly acid, neutral, and mildly alkaline, respectively, in sterile buffered water for a period of 30 days at 25°C (EPA, 1995). Sampling for breakdown products and the remaining concentration of parent material occurs at frequent intervals. Due the potential effects of buffer concentration, these hydrolysis studies are usually run at two separate buffer concentrations, which are usually 0.001 and 0.01 Molar.

Triclopyr TEA is very soluble in water and immediately dissociates to the triclopyr conjugate base. Therefore, triclopyr acid is immediately available as a contact herbicide dissolved in the water column. Since triclopyr acid is not hydrolyzed, it remains available as a contact herbicide until it is removed from the water by other physical or biological methods (photolysis, sorption to soil, sorption to sediment, sorption to plant material or biological breakdown by microorganisms).

3.2.1 Half-life

The EPA RED (1998) reviewed triclopyr environmental fate literature. They cited early references indicating that triclopyr acid is stable in water. Triclopyr acid is removed from water primarily by photolysis and microbial degradation. However, since sunlight is extensively absorbed by the ambient plant cover and dissolved organic material, it seems likely that microbial degradation, advection and dispersion are the primary means by which triclopyr is dissipated from the water column (Woodburn et al, 1993). However, photolysis can contribute substantially to the degradation of triclopyr acid, triclopyr TEA and triclopyr BEE. These three triclopyr products are degraded rapidly under natural sunlight (0.6 to 6.6 days) with both the dominant degradate and degradation rate varying somewhat with the product tested (EPA RED, 1998). See Section 3.3 for a detailed discussion of the photolysis of triclopyr.

Table 3.2 illustrates the pH-dependency of triclopyr acid, triclopyr TEA and triclopyr BEE. The rate of hydrolysis for triclopyr acid and triclopyr TEA could not be measured because it does not significantly hydrolyze in buffered water at pHs 5, 7 and 9. No degradation of triclopyr acid or triclopyr TEA was seen during the course of various studies (EPA RED, 1998). However, triclopyr TEA was seen to dissociate to the conjugate base within one minute of application to water. Since the pKa of triclopyr acid is 2.93, it will also dissociate completely and fairly rapidly to the triclopyr conjugate base at pHs greater than 5.0. If it occurs, the hydrolysis half -life can be predicted by the following pseudo first-order rate equation:

$T(1/2) = 0.693/(K_b)$
where K_b = pseudo first order hydrolysis rate constant (day^{-1})

Since the [$^{-}$OH] concentration is high, relative to the concentration of triclopyr acid, its concentration can be ignored.

Since triclopyr acid and triclopyr TEA do not readily hydrolyze, the pseudo first order hydrolysis rate constant is essentially zero at pHs between 5.0 and 9.0. The pH of most natural waters is approximately 6 to 9, particularly during the summer months, therefore, triclopyr TEA can be expected to degrade very slowly, if at all, due to hydrolysis when applied to lakes and ponds. It is possible that the bacteria associated with the water column and sediment may be able to degrade triclopyr TEA after it has been transformed to triclopyr acid.

Triclopyr BEE hydrolyzes to triclopyr acid and 2-butoxyethanol (BEOH) at rates controlled by the pH and temperature of the surrounding water and the concentration of buffer (phosphate or borate) present. At 25°C and a buffer concentration of 0.01 M, the half-life of triclopyr BEE was 84.0, 8.7 and 0.3 days at pH 5, 7 and 9, respectively (EPA RED, 1998 and Bidlack, (no date) in McCall and Gavit, 1986). The rate of hydrolysis for triclopyr BEE to triclopyr acid plus BEOH increases by two- to four-fold for every 10°C increase in temperature in the range of 15° to 35°C. Similar temperature effects were seen between 35° and 54°C in converting the butoxyethyl ester of triclopyr to triclopyr acid plus the associated alcohol (Szeto, 1993). Buffer catalysis effects are seen at concentrations of buffer that are higher than 0.001 M (Szeto, 1993). However, since potential buffer concentrations in most aquatic environments seldom exceed 0.001 M, buffer catalysis is not expected to be significant. In natural water with unbuffered pHs around 6.7, triclopyr BEE hydrolyzes to triclopyr acid plus the associated alcohol in 0.5 to 11.7 days (McCall et, al, 1988 and Szeto et al, 1993). At low pHs (pH 4.5) small amounts of the toxic metabolite 3,5,6-trichloro-2-pyridinol (TCP) are formed from the hydrolysis of triclopyr BEE. It is not clear if low pHs will degrade triclopyr BEE, triclopyr TEA or triclopyr acid to TCP but it seems likely that this hydrolysis will occur at low pHs when triclopyr BEE is the reactant. However, formation of TCP usually occurs due to the action of bacteria that can degraded triclopyr, since pHs below 6.0 are uncommon in natural water bodies. Although triclopyr BEE is fairly toxic to salmonids and other fish (LC50 = 0.45 to 2.4 ppm), the triclopyr acid and the TCP metabolite are typically 10- to 100-fold less toxic (LC50 of TCP = ~1.5 to 12.65 ppm; LC50 of triclopyr acid = 117 to 148 ppm according to EPA, or 5.3 to 9.7 ppm according to Wan et al, 1987). Such natural hydrolysis processes can significantly decrease the aquatic toxicity of organic triclopyr esters, since the aquatic toxicity of triclopyr acid and triclopyr TEA is LC50 = 22 to 439 ppm a.e. (See Section 4 for Triclopyr). Triclopyr BEE hydrolyzes rapidly in water with pHs higher than ~7.0 (DT50 = 0.5 to 11.7 days); degradation half-lives of triclopyr BEE in sterile water with similar pH and low buffer strength are about the same as those seen in natural water. Hydrolysis of triclopyr BEE to triclopyr acid on sediment is very rapid (DT50 = ~0.1 days). Information on the hydrolysis of triclopyr esters like triclopyr BEE are provided as historical reference points. At this time, these products are not used to control fully aquatic submerged or emerged weeds. However, after the triclopyr has become completely distributed within the water column and sediment by advection, dispersion and a certain minimal amount of adsorption, the system half-life for triclopyr acid, triclopyr TEA and triclopyr BEE is typically around 46 days (Wauchope et al, 1992). However, field work in Green et al (1989), Getsinger et al (2000), Petty et al (1998), Getsinger et al (1997) and the EPA RED (1998) indicate that both water and sediment half-lives range from less than one day to approximately 7.5 days.

3.2.2 Degradation products

There are no significant degradation products with herbicidal action due to the hydrolysis of triclopyr acid, triclopyr TEA or triclopyr TEA at pH 5, 7, and 9. However, triethylamine (TEA) and 2-butoxyethyl alcohol (BEOH) as well as TCP produced at low pHs may remain in the water column for short periods of time.

TEA found in water at 1.33 ppm is not degraded by microbes in aerobic sediment/water systems for up to 14 days but by the 18th day 50% of TEA has been metabolized to carbon dioxide and 25 % may be bound to the sediment. In anaerobic sediment/water systems, similar concentrations of TEA may remain in this system with a half-life of up to 2 years. The TEA distributes itself equally between the water and sediment extracts with 10% to 19% of the detectable residue binding to the sediment.

BEOH has a very short half-life in aerobic water/sediment. ^{14}C-BEOH at concentrations of 4.0 ppm is converted to 2-butoxyacetic acid with a half-life of approximately 3 days. This intermediate metabolite (2-butoxyacetic acid) has a half-life of about 1 day. Sixty-nine percent of the ^{14}C-BEOH was mineralized to carbon dioxide within 10 days. Under anaerobic water/sediment conditions, BEOH is metabolized to 2-butoxyacetic acid with a half-life of 1.4 days at 25°C, and this intermediate metabolite has a half-life of 73.3 days. Under anaerobic water/sediment conditions 57.4% of the applied ^{14}C-label is mineralized to carbon dioxide in 193 days.

If TCP is produced by hydrolysis at low pH, it may be degraded by photolysis or by microbes (particularly, *Pseudomonas* sp.) (Dilling et al, 1984 and Feng et al, 1997). TCP has a photolysis half-life of 120 minutes in river water at 1-meter depth when the water is pH = 7.0 and the latitude is 40° North. In soils TCP at concentrations of 5 ppm is degraded by *Pseudomonas* sp. to a variety of metabolites within 4-days. However, at high concentrations (>100 ppm), TCP is toxic to several species of microbes. If *Pseudomonas* sp. is exposed to 100 ppm TCP, it takes approximately three weeks to completely degrade. However, *Pseudomonas* sp. was not observed to degrade TCP when the exposure concentration was 200 ppm (Feng et al, 1997). In similar work, Racke et al (1988) found that TCP was readily degraded at 5 ppm with 80% of the applied label mineralized in 2 weeks. However, 50 ppm TCP largely inhibited mineralization by microbes with only 4 percent of the applied label being mineralized in 2 weeks. TCP has considerable antibacterial activity at 100 ppm and almost completely inhibits the microbial degradation of the insecticides, isofenphos and carbofuran.

Table 3.2
Hydrolysis of Triclopyr (Laboratory Studies)

Matrix	Compound	pH	Temp	Half-life (DT_{50})	Observed Product of Hydrolysis and Notes	Reference
Sterile buffered water*	Triclopyr acid	5	~25°C	Very long Cannot be measured. No degradation in 30 days	None	EPA RED, 1998; Cleveland a& Holbrook, 1991 in Getsinger et al, 2000
Sterile buffered water*	Triclopyr acid	7	~25°C	Very long Cannot be measured. No degradation in 30 days	None	EPA RED, 1998; Cleveland a& Holbrook, 1991 in Getsinger et al, 2000
Sterile buffered water*	Triclopyr acid	9	~25°C	Very long Cannot be measured. No degradation in 30 days	None	EPA RED, 1998; Cleveland a& Holbrook, 1991 in Getsinger et al, 2000
Sterile buffered water*	Triclopyr BEE	5	~25°C	84 days	Triclopyr acid and possibly BEOH	EPA RED, 1998
Sterile buffered water*	Triclopyr BEE	7	~25°C	8.7 days	Triclopyr acid and possibly BEOH	EPA RED, 1998
Sterile buffered water*	Triclopyr BEE	9	~25°C	0.3days	Triclopyr acid and possibly BEOH	EPA RED, 1998
Natural water from the Black Creek, Michigan*	Triclopyr BEE	6.7	~25°C	0.5days	Triclopyr acid and possibly BEOH	EPA RED, 1998 & McCall et al, 1988
Sterile Buffered water (0.2M phosphate	Triclopyr BEE (1.0 ppm)	5.0	15°C 25°C 35°C	8.7 days 3.5 days 1.1 days	Triclopyr acid and possibly BEOH	McCall et al , 1988
Sterile Buffered water (0.2M phosphate	Triclopyr BEE (1.0 ppm)	7.0	15°C 25°C 35°C	1.1 days 0.36 days 0.096 days	Triclopyr acid and possibly BEOH	McCall et al , 1988
Sterile Buffered water (0.2M phosphate	Triclopyr BEE (1.0 ppm)	9.0	15°C 25°C 35°C	0.020 days 0.0063 days 0.0025 days	Triclopyr acid and possibly BEOH	McCall et al , 1988

Table 3.2
Hydrolysis of Triclopyr (Laboratory Studies) (continued)

Matrix	Compound	pH	Temp	Half-life (DT_{50})	Observed Product of Hydrolysis and Notes	Reference
Sterile buffered water (0.01 M phosphate)	Triclopyr BEE (10.0 ppm)	7.0	35°C 40°C 45°C 52°C 54°C	3.0 days 2.1 days 1.3 days 0.58 days 0.55 days	Triclopyr acid and possibly BEOH	Szeto, 1993
Sterile buffered water (0.01 M phosphate)	Triclopyr BEE (10.0 ppm)	4.5 5.5 6.5 6.6	35°C 35°C 35°C 35°C	79.5 days 54.7 days 8.3 days 7.0 days	Triclopyr acid, TCP at pH 4.5 and possibly BEOH	Szeto, 1993
Sterile buffered water (0.001 M phosphate)	Triclopyr BEE (10.0 ppm)	6.6	35°C	10.3 days	Triclopyr acid and possibly BEOH	Szeto, 1993
Capilano River water (Hardness = 6.0 ppm & conductivity = 14 mhos	Triclopyr BEE (10.0 ppm)	6.6	35°C	11.7 days	Triclopyr acid and possibly BEOH	Szeto, 1993
Buffered Capilano water (0.01 M phosphate)	Triclopyr BEE (10.0 ppm)	7.0 7.5 7.6	35°C 35°C 35°C	3.0 days 1.0 days 0.72 days	Triclopyr acid and possibly BEOH	Szeto, 1993
Buffered Capilano River water (0.002 M phosphate)	Triclopyr BEE (10.0 ppm)	7.6	35°C	2.0 days	Triclopyr acid and possibly BEOH	Szeto, 1993
Tamihi Creek water (hardness = 24 ppm & conductivity = 53 mhos)	Triclopyr BEE (10.0 ppm)	7.6	35°C	1.7 days	Triclopyr acid and possibly BEOH	Szeto, 1993
buffered Tamihi Creek water (0.01 M phosphate)	Triclopyr BEE (10.0 ppm)	8.0	35°C	0.45 days	Triclopyr acid and possibly BEOH	Szeto, 1993
buffered Tamihi Creek water (0.01 M borate)	Triclopyr BEE (10.0 ppm)	8.5	35°C	0.18 days	Triclopyr acid and possibly BEOH	Szeto, 1993

Table 3.2
Hydrolysis of Triclopyr (Laboratory Studies) (continued)

Matrix	Compound	pH	Temp	Half-life (DT$_{50}$)	Observed Product of Hydrolysis and Notes	Reference
Sterile buffered water (0.01 M phospahte	Triclopyr BEE (10.0 ppm)	4.5	35°C	<252 days Calculated half-life for triclopyr BEE = 78 days Calculated half-life of triclopyr BEE plus triclopyr acid = 790 days	After 252 days of incubation there was 10.8% triclopyr BEE, 67.1% triclopyr acid and 22.1% TCP	Szeto, 1993
Hydrolysis on Soil	Triclopyr BEE (1.0 to 1.5 ppm)	5.4	25°C	Silty clay loam 0.1 days	Hydrolysis of triclopyr BEE to triclopyr acid on soil is very rapid	McCall et al, 1988
		6.1	25°C	Silt loam 0.096 days		
		6.8	25°C	Sandy loam 0.092 days		

* EPA guideline study

3.3 AQUEOUS PHOTOLYSIS

<u>Summary</u>: *Most authors believe that triclopyr TEA, triclopyr BEE and triclopyr acid and the toxic degradate TCP are rapidly degraded by spring, summer and fall sunlight (Woodburn et al, 1993; Getsinger et al, 2000; McCall and Gavit, 1986; and EPA RED, 1998). However, a few authors believe that triclopyr and TCP are not readily degraded by photolysis due to extensive quenching in water more than 15 cm in depth (Getsinger et al, 2000). However, it has been seen that removal of aquatic weeds with triclopyr improves the penetration of light to lower depths (Petty et al, 1998). Factors that can influence the rate of aqueous photolysis include vegetative cover, type of vegetation, depth of the plot, suspended matter and whether that suspended matter quenches sunlight or acts as a sensitizer and increases the rate of photolysis. Although aqueous photolysis is probably an important factor in degrading triclopyr, photolysis on soil has not been demonstrated to be a significant factor in the degradation of triclopyr acid. The EPA (EPA RED, 1998) is currently evaluating photolysis studies for triclopyr acid on soil. Soils can impact the rate of photolysis of pesticides in many ways. A few of the processes that may influence the rate of photolysis for pesticides on soil include: quenching, photosensitization, radical reactions, light screening, and effects of altering organic content, soil particle size and temperature (Miller and Zepp, 1983). However, the effects of these processes are not well understood.*

The degradates produced by aqueous photolysis vary depending on the triclopyr product that is photolyzed and the source of the water. For example, triclopyr acid (which may be formed either after the almost instantaneous dissociation of triclopyr TEA, or *hydrolysis of triclopyr BEE) is photolyzed to 5-chloro-3,6-dihydroxy-2-pyridinyloxyacetic acid (MDPA), and oxamic acid. In sterile buffered water (pH 7), the main degradate is MDPA with 48% of the applied ^{14}C-label degraded to MDPA after ~13 hours of exposure to natural sunlight (August in Michigan). In sterile buffered water, a small amount of oxamic acid (2.8% of the applied ^{14}C-label) is produced after ~13 hours of exposure to natural light. Small amounts of carbon dioxide (<0.1%) were produced after irradiation of sterile buffered water but no other significant degradates were seen after irradiation of triclopyr acid (EPA RED, 1998 and Woodburn et al, 1993).*

In natural river water, oxamic acid is the predominant degradate with 16% of the applied ^{14}C-label degraded to oxamic acid after exposure to 54 hours of natural light (EPA RED, 1998 and Woodburn et al, 1993) and small amounts of MDPA (5.4% of the applied ^{14}C-label) were produced. Small amounts of carbon dioxide (<0.1%) were produced after irradiation of natural river water. A number of low molecular weight organic acids have been tentatively identified as minor photolysis products. These include oxalic acid, pyruvic or maleic acid and malic or 2-chlorosuccinic acid. Although these acids were tentatively identified by comparison of their retention times with known standards, it was not possible to confirm these structures by mass spectral analysis. Furthermore, the concentrations of these low molecular weight acids could not be determined accurately even though their combined concentration was significant [(~50% of the applied ^{14}C-label (EPA RED, 1998 and Woodburn et al, 1993)].

Since triclopyr TEA and triclopyr BEE rapidly transform to triclopyr acid, no soil photolysis studies are required by the EPA for these products. The photolysis of triclopyr acid is described above after it has dissociated from triclopyr TEA or hydrolyzed from triclopyr BEE. However, some work has been done on the photolysis of triclopyr BEE at pHs of ~5.0, where it is most stable to hydrolysis. The photo-products after 30 days of irradiation on a sterile buffered solution containing 1.0 ppm triclopyr BEE included 17% (5/6)- chloro-3-hyroxy-s-pyridine and 6% 2-hydroxyethyl dichloropyridinyloxyacetate. At least 15 other non-volatile compounds were isolated at 10% of the applied ^{14}C-label. Organic volatiles were 1.6% of the applied radiation. These photoproducts appear to be degraded rapidly by microbes with 29% of the applied ^{14}C-label being mineralized to carbon dioxide in 30 days.

The microbial metabolite of triclopyr acid is 3,5,6-trcloro-2-pyrdinol (TCP) is photodegraded to five compounds containing intact pyridine rings and six low molecular weight alkenes. These products may not be germane to real environmental conditions since a high intensity lamp [(30W, 254nm, 0.5 W/ft^2), 18.5 inches from the photolysis vessel)] was used to generate these degradates. 85.1% of the chloride was released after 6 hours exposure to this light source. These photolysis products are ultimately degraded to carbon dioxide, water and ammonium ion by the microbe, Pseudomonas *sp. After 2-hours of photolysis and 4 hours of incubating these TCP photo-products with resting cell cultures of* Pseudomonas *sp., 22.9% of the applied ^{14}C-TCP was recovered as carbon dioxide, 54.2% remained in the incubation medium and 2.3% was incorporated into the microbial biomass (Feng et al, 1998). Although, TCP is degraded rapidly by artificial sunlight (313 nm), the nature of the degradates produced by this photolysis is not clear (Dilling et al, 1984).*

It is unclear what, if any, impact that photolysis would have on triclopyr acid, triclopyr BEE or TCP when they are sorbed onto soil surfaces. Soil photolysis studies are currently under review at the EPA (EPA RED, 1998). It is known that soils can quench, *photosensitize, produce radical reactions, or screen out impinging light. However, the effect of organic content, soil particle size and temperature are not well understood. These processes are known to change the rate of photolysis of other pesticides on soils (Miller & Zepp, 1983).*

The photolytic half-life of triclopyr acid is generally less than 1 day at 40° to 50°C North latitude during the months when triclopyr TEA might be used for the control of aquatic weeds. Triclopyr BEE has a much longer photolytic half-life and generally ranges between 3.5 and 7.5 days at 40° to 50° North Latitude during the months when triclopyr BEE might be used for the control of noxious non-aquatic weeds. However, triclopyr BEE is not registered for the control of fully aquatic, submerged, floating or emerged weeds. Half-lives of triclopyr in buffered water have generally been seen to be somewhat longer under summer sunlight at 40° N Latitude than under artificial sunlight with similar intensities. Also the photolysis half-lives of triclopyr are usually somewhat longer in natural river water than in sterile buffered water. Typically, the half-life of triclopyr under natural sunlight is ~2-fold longer than under artificial light with a similar intensity and the photolysis half-life in natural water is ~2-fold longer than in sterile buffered water (Woodburn et al 1993; McCall and Gavit, 1988 and EPA RED, 1998).

Photolysis testing is carried out in a laboratory. Vessels containing solutions of the herbicide in sterile distilled or deionized and buffered water are irradiated with either a mercury vapor lamp or natural sunlight. Identical vessels are kept in the dark for the duration of the study and also sampled in order to compensate for the effects of any hydrolysis occurring. Testing is usually carried out at 25°C, at pH 5, 7 and 9. Other photolysis testing, such as photolysis of a pesticide on the surface of a soil, is also required for products that might be deliberately or incidentally applied to soil, as is the case for triclopyr TEA and triclopyr BEE. However, because triclopyr TEA and triclopyr BEE dissociate or hydrolyze to triclopyr acid almost immediately after application to soil, photolysis studies on soil are only required with triclopyr acid (EPA RED, 1998).

The purpose of photolysis experiments is to isolate the effect of sunlight, specifically the ultraviolet and near-ultraviolet part of the spectrum, on the degradation of an herbicide without biological or chemical interactions. Natural sunlight's visible spectrum covers wavelengths from about 800 nm (deep red) to about 300 nm (deep violet). Generally speaking, only light in the violet and ultraviolet end of the spectrum has enough energy to initiate or influence chemical reactions (photochemical reactions). Air, as well as ozone, strongly filters near-ultraviolet and ultraviolet radiation, and cuts off nearly all radiation below 290 nm wavelength. Water is transparent to radiation down to approximately 180 nm (far ultraviolet), assuming that there are no suspended solids or dissolved colored material such as humic acids to impair passage of the light. Aqueous photolysis experiments done under natural sunlight are influenced by the season, latitude, time of day, depth of the water column and ozone thickness (Zepp and Cline, 1977). The State of Washington is located between 40 and 50° North Latitude. Therefore, this review of photolysis mainly concentrate on studies run at these latitudes. Although photolysis is considered by most authors to be an important factor in the degradation of triclopyr and its metabolite TCP, some authors (Getsinger et al, 2000 and Petty et al, 1998) believe that photolysis is not an important factor in the degradation of triclopyr and TCP at depths below 15 cm.

3.3.1 Half-life

Table 3.3 summarizes photolysis data for triclopyr acid, triclopyr BEE and TCP. Photolysis testing is normally carried out with triclopyr acid, and only a few studies were found that addressed triclopyr BEE. Since triclopyr BEE is not registered for use on fully aquatic weeds, its photolysis data is presented primarily for comparative purposes. Triclopyr BEE has a much longer photolysis half-life than triclopyr acid. The photolysis half-life for triclopyr acid, which is the dissociation product of triclopyr TEA, ranges from ~ 2 days in natural river water to less than one day in sterile buffered water exposed to natural sunlight at 40° to 50° North Latitude. Triclopyr BEE has been seen to have a longer half-life than triclopyr TEA under similar conditions. For example, the half-life of triclopyr BEE was typically 2 to 7.5 days in sterile buffered water when exposed to simulated sunlight similar to natural light at 40° to 50° North Latitude. However, under natural California sunlight (~30° North Latitude), the photolysis half-life for triclopyr BEE was 6.6 days. It seems likely that triclopyr TEA, which rapidly dissociates to triclopyr acid, should be degraded and detoxified by photolysis particularly at the surface of the water column. Triclopyr TEA should also be degraded and detoxified by photolysis in water of 1-meter depth.

The decreased rate of photolysis in natural waters is probably due to a small degree quenching effects in natural water. Quenching can be caused by the presence of seston (algae, and sediment particles) and the presence of dissolved organic (humic acids and fulvic acid) and inorganic materials (Woodburn, 1993).

Since levels of the microbial metabolite (TCP) can be high in water (0.020 ppm), it is important to determine its photolysis half-life. TCP is a metabolite that the EPA considers having toxicological significance in the environment. TCP has a very short half-life in artificial sunlight with intensity similar to natural sunlight at 40° North Latitude. The longest half-life for TCP in river water exposed to summer sun at 1 meters depth should not be longer than 2 hours. TCP exposed in sterilized buffered water at the surface of the water column has a half-life of 0.073 hours. Therefore, it seems likely that TCP will be degraded and detoxified by photolysis under natural conditions.

Environmental characteristics, such as degree on cloud cover, season, latitude and ozone thickness can impact the rate of degradation and half-life of a pesticide exposed to sunlight. However, experimental parameters such as the type of buffers used and the size and depth of the photolysis chamber may also influence the rate of degradation. The amount of plant cover has been hypothesized to decrease the rate of photolysis since it impacts the depth to which near UV and UV light can penetrate (Petty et al, 1998). In general, the rate of photolysis can be impacted by algae or algal exudates by quenching which slows photolysis down or by photo-activation which may increase the rate of photolysis and change the dominant degradate. Similar changes in the degradation rate can be affected by the presence of small amounts of organic and inorganic matter. To eliminate the laboratory effects that are not due to photolysis, all other parameters should be kept constant; particularly, oxygen content, pH, buffer concentration, and organic and inorganic matter content. Since triclopyr acid is not susceptible to hydrolysis, the pH of the photolysis solution is usually kept at ~7.0. However, since triclopyr BEE is subject to hydrolysis to triclopyr acid at pHs of 7 and 9 but not at pH of 5, a pH of 5 for the photolysis solution should be maintained when testing triclopyr BEE for non-hydrolytic effects (EPA RED, 1998).

Studies on the photo-degradation of triclopyr TEA and triclopyr BEE on soil are not required since these products are rapidly transformed to triclopyr acid when they are in contact with soil. The photolysis of triclopyr acid on soils is currently being reviewed by EPA (EPA RED, 1998). However, currently no data is publicly available on the photo-degradation of triclopyr acid on soil. Soils may influence the rate of photolysis of herbicides by quenching, photosensitization, radical reactions, or light screening and the effects of organic content, soil particle size, temperature and moisture content, which are currently not well understood but may influence the rate at which a herbicide is degraded by sunlight (Miller and Zepp, 1983).

Data indicates that since the hydrolysis and vapor half-lives are very long other mechanisms may be more significant in the degradation and dissipation of triclopyr from the aquatic environment. While photolysis may be important for the degradation of triclopyr in shallow, non-turbid waters with low levels of weed growth, it is likely that microbial degradation, and possible adsorption into target plants, are the major modes of dissipation in the field. Since triclopyr is not readily adsorbed by soil or sediment, this seems an unlikely mode for the dissipation of triclopyr, particularly triclopyr TEA and triclopyr acid. However, triclopyr BEE may be dissipated and inactivated in soils that contain high amounts of organic matter. Nevertheless, since triclopyr BEE is rapidly transformed to triclopyr acid on most soils, it seems unlikely that triclopyr BEE would be adsorbed to soil/sediment prior to this transformation (Jotcham et al, 1989).

The principal photolytic degradate varies with formulation and water type. Triclopyr TEA is degraded primarily (~50% under natural sunlight) to 5-chloro-3,6-dihydroxy-2-pyridinyloxyacetic acid (MDPA) in sterile pH 7 buffered water. However, in natural river water, oxamic acid and not MDPA is the dominant metabolite [16.4 % of the ^{14}C-label is degraded to oxamic acid after 54 hours of exposure (Woodburn et al, 1993)]. Triclopyr BEE in pH 5 water is degraded to 17% (5/6)-chloro-3-hydroxy-s-pyridinone and 6% 2-hydroxethyl ester of dichloropyridinyloxyacetic acid, and 29.4% carbon dioxide after 30 days of exposure to natural outdoor light in California. Fifteen other non-volatile degradates constituting 10% of the applied radiolabel were also produced from the photolytic degradation of triclopyr BEE. Small amounts of organic volatiles (<2% of the applied labels) were formed during the photolysis of triclopyr BEE (EPA RED, 1998).

TCP is a product of microbial degradation that is subject to photolysis and further degradation by the bacteria *Pseudomonas* sp. Although TCP is known to be degraded rapidly in sunlight (0.073 to 2 hours in summer sunlight), the degradants that have been studied were formed by exposure to a UV wavelength (254 nm) that is not found in sunlight. This wavelength released 85% of the chlorine present in TCP by reductive dechlorination. With the final product being 2-hydroxypyridine in equilibrium with 2-ketopyridine. From here ring cleavage occurs which eventually leads to the production of carbon dioxide, water and ammonium ion. Alternatively, chlorine may be retained as the pyridinone ring cleaves, producing 4-carbon straight chain alkenes with a triple-bonded nitrogen at one end of the molecule. Since the wavelength (254 nm) used to generate these metabolites is not found in sunlight, it is unclear if these degradates would be produced when TCP is exposed to natural light. After photolysis has occurred, resting cell cultures of *Pseudomonas* sp. are known to convert 22.9% of the radiolabel to carbon dioxide and incorporate 2.3 % or the radiolabel into the biomass of this microbe. Fifty-four percent of the labeled chemical remains in the microbial incubation medium after 4 hours (Feng et al, 1998).

3.3.2 Degradation products

The EPA RED (1995) and Woodburn et al (1993) found that the major product produced during photolysis of triclopyr acid (dissociated triclopyr TEA) in sterile buffered water was MDPA. MDPA was also the only significant photolysis product produced in sterile pH 7 buffered water. After 13 hours of photolysis under natural sunlight, 47.7% of the radiolabel was recovered as MDPA. Small amounts of oxamic acid (2.8%) and carbon dioxide (<0.1%) were also recovered.

In natural river water from the Chippewa and Tittabawassee river confluences, the main degradate of triclopyr acid was oxamic acid. After 54 hours of exposure to natural sunlight (August in Michigan), the main degradate was oxamic acid (16.4%). Minor amounts of MDPA (5.4%) and carbon dioxide (0.1%) were also recovered after photolysis of triclopyr acid for 54 hours. In this river water, 3 low-molecular weight organic acids were seen as minor products. These products were tentatively identified as oxalic acid, pyruvic or malic acid, and maleic or 2-chlorosuccinic acid. Although none of these low molecular weight organic acids were considered to be more than minor products, their combined concentration was approximately 50% of the applied ^{14}C-label (Woodburn et al, 1993).

The photolysis of triclopyr BEE may be only interesting at the intellectual level. Triclopyr BEE should form the same photolysis products after hydrolysis to triclopyr acid and 2-butoxyethanol (BEOH) that are produced after photolysis of triclopyr acid (the dissociation product of triclopyr TEA). However, if photolysis of triclopyr BEE is studied at pH 5, there is no direct hydrolysis. At this low pH, the primary photolysis products are different than those produced from the photolysis of triclopyr acid or triclopyr TEA. If hydrolysis does not occur, the primary photolysis products of triclopyr BEE after 30 days of irradiation with California sunlight are (5/6)-chloro-3-hydroxy-s-pyridinone (17%), 2-hydroxyethyl ester of dicloropyridinyloxyacetate (6%). At least 15 additional non-volatile organic products were isolated at <10% of the applied radiation but none were identified. Approximately 1.6% of the applied radiation consisted of volatile organic products (EPA RED, 1998).

TCP (3,5,6-trichloro-2-pyridinol), a microbial metabolite of triclopyr is also rapid photolyzed with a DT50 that is two hours or less in river water exposed to summer sunlight at 40° North Latitude. The DT50 is defined as the time it takes for 50% of the applied test substance to degrade to other chemicals. During the winter months the half-life of TCP in pure water at the top of the water column would be expected to be only 0.25 hours. Although 85.1% of the chloride was released by exposure to 254 nm monochromatic light for 6 hours, it is unclear if this would occur after exposure to natural sunlight. TCP can apparently be degraded by two separate photolysis mechanisms. One mechanism is reductive dechlorination with a final ring opening of 2-hydroxypyridine to form a four-carbon oxamate aldehyde with further degradation to carbon dioxide, water and ammonium ion. Chlorine can alternatively be retained as the ring cleaves into a number of low molecular weight alkenes with a triple-bonded nitrogen at one end of the molecule. A *Pseudomonas* culture can extensively degrade TCP photoproducts when the incubation time is 4 days. 22.9% of the applied radiation degraded to carbon dioxide in 4 days and 2.3% of the applied radiation is incorporated into the biomass of the *Pseudomonas* sp. culture. However, 54% of the applied radiation remains in the incubation medium and has not been further characterized (Dilling et al, 1984 and Feng et al, 1998.) It was also noted that this *Pseudomonas* species could use TCP as a sole carbon-energy source. Presumably, this *Pseudomonas* sp. can also use most TCP photolysis products as a carbon-energy source although this is not entirely clear. However, it is clear that the dichlorodihydroxypyridines cannot be used as a carbon-energy source or be degraded by *Pseudomonas* sp. (Feng et al, 1997 and Feng et al, 1998).

It has been suggested that photochemostats and biofilms can be used in combination to degrade TCP and possibly triclopyr that has gotten into a water body or water treatment plant prior to the outfall. However, this remediation method is only a hypothesis and no definitive work has been conducted to demonstrate the feasibility of this methodology.

Research on the photolysis of triclopyr TEA and triclopyr BEE on soil has not been required by the EPA since these products are rapidly transformed to triclopyr acid. However, the results of photolysis studies with triclopyr acid are currently being evaluated by the EPA (EPA RED, 1998). Half-lives of triclopyr acid on soil and the metabolites produced on soils treated with triclopyr acid are currently not publicly available. It is unclear whether triclopyr acid will photolyze significantly on soil since many factors contained in soil may influence the rate at which triclopyr acid is photolytically degraded. Photo-excitement of pesticides may be influenced by pigments in the soil. These pigments may also photosensitize the system and make it more likely that degradation of the pesticide due to photolysis will occur. Other factors affecting soil photolysis may include soil moisture, soil particle size (blocking of light by soil grains), interference by organic matter in soil, soil mineral base, and soil light adsorbing characteristic. No model exists for assessing the importance of photolysis on soil surfaces. The processes of quenching, photosensitization, radical reactions, light screening and effects of organic content, soil particle size, temperature and moisture are not well understood (Miller and Zepp, 1983). Photolysis of triclopyr acid also occurs on the surfaces of plants treated with triclopyr. The rate of degradation is related to the intensity of the sunlight falling on the foliage of treated plants. This phenomenon could occur on treated crop plants and on floating and emergent weeds that may be treated with triclopyr. Any triclopyr bound to dead and dying, floating or emerged plant debris may be exposed to sunlight leading to photodecomposition before it is incorporated into soil or sediment. Any triclopyr reaching soil or sediment either directly or released from incorporated organic materials (decaying plant material) is subject to adsorption and potential protection from photo-degradation. In natural systems, photochemical reactions may compete with adsorption and microbial decomposition and are likely to be comparatively slow. The avenues of loss of triclopyr in soils and sediment seem to be through photochemical and microbial degradation as well as adsorptive processes. Since sorptive capacity and sorption itself tends to low, it is likely that triclopyr and TCP will not accumulate in soils.

Table 3.3
Photolysis of Triclopyr (Laboratory Studies)

Matrix	**Compound**	**Initial Conc**	**pH**	**Temp (°C)**	**Other conditions**	**Half-life (DT_{50})**	**Reference**
Sterile buffered water (mid summer sun)	Triclopyr TEA; since pKa = 2.7, triclopyr exists primarily as triclopyr acid	n.r.[1]	5 to 9	Probably around ~25°C	Midsummer sun	2 hours	Hamaker n.d. in McCall and Gavit, 1988
Sterile buffered water at 35°C (Filtered Artificial sunlight = 313 nm)	Triclopyr acid	1.40 ppm	5.2	~35°C	NR	5.4 hours	McCall and Gavit, 1988
Sterile buffered water at 35°C (Filtered Artificial sunlight = 313 nm)	Triclopyr acid	1.40 ppm	5.2	35°C	40° North midday sun (estimate based on laboratory studies) Spring surface Spring 1 meter Summer surface Summer 1 meter Fall surface Fall 1 meter Winter surface Winter 1 meter	 2.8 hours 3.7 hours 2.1 hours 2.8 hours 4.6 hours 6.2 hours 10.6 hours 14.1 hours	McCall and Gavit, 1988

Table 3.3
Photolysis of Triclopyr (Laboratory Studies) (continued)

Matrix	Compound	Initial Conc	pH	Temp (°C)	Other conditions	Half-life (DT_{50})	Reference
Sterile buffered water at 35°C (Filtered Artificial sunlight = 313 nm)	Triclopyr acid	1.40 ppm	5.2	35°C	Integrated intensity values for a day 30°N Spring 30°N Summer 30°N Fall 30°N Winter	Estimates based on laboratory testing 12.0 hours 12 .0 hours 16.8 hours 19.2 hours	McCall and Gavit, 1988
Sterile buffered water at 35°C (Filtered Artificial sunlight = 313 nm)	Triclopyr acid	1.40 ppm	5.2	35°C	Integrated intensity values for a day 40°N Spring 40°N Summer 40°N Fall 40°N Winter	Estimates base on laboratory testing 14.4 hours 12 .0 hours 21.6 hours 40.8 hours	McCall and Gavit, 1988
Sterile buffered water at 35°C (Filtered Artificial sunlight = 313 nm)	Triclopyr acid	1.40 ppm	5.2	35°C	Integrated intensity values for a day 50°N Spring 50°N Summer 50°N Fall 50°N Winter	Estimates base on laboratory testing 19.2 hours 14.4 hours 38.4 hours 132.0 hours	McCall and Gavit, 1988
Sterile buffered water (Natural light)*	Triclopyr acid	n.r.[1]	7.0	~25°C	August in Michigan	14.4 hours	EPA RED, 1998
Sterile buffered water (Artificial light)*	Triclopyr acid	n.r.[1]	7.0	~25°C	Artificial light	8.7 hours	EPA RED, 1998

Table 3.3
Photolysis of Triclopyr (Laboratory Studies) (continued)

Matrix	**Compound**	**Initial Conc**	**pH**	**Temp (°C)**	**Other conditions**	**Half-life (DT_{50})**	**Reference**
Natural river water (Natural light)*	Triclopyr acid	n.r.[1]	7.0	~25°C	August in Michigan	40.8 hours	EPA RED, 1998
Natural river water (Artificial light)*	Triclopyr acid	n.r.[1]	7.0	~25°C	Artificial Sunlight	16.8 hours	EPA RED, 1998
Buffered sterile water*	Triclopyr acid	n.r.[1]	7.0	~25°C	n.r.	12.0 hours	Woodburn et al, 1990 in Getsinger et al, 2000 & Woodburn et al, 1993
Natural river water*	Triclopyr acid	n.r.[1]	NR	~25°C	Midsummer sunlight at 40°North	28.8 hours	Woodburn et al, 1990 in Getsinger et al, 2000
Buffered Sterile water*	Triclopyr acid	9.8 uM	7.0	~25°C	Artificial light (280 to 350 nm)	8.64hours	Woodburn et al, 1993
Buffered Sterile water*	Triclopyr acid	9.8 uM	7.0	~25°C	Midland Michigan August sunlight	14.4 hours	Woodburn et al, 1993
Chippewa and Tittabawassee River Confluence (MI)*	Triclopyr acid	9.8 uM	7.0-8.0	25°C	Artificial light (290 to 350 nm)	17.0 hours	Woodburn et al, 1993
Chippewa and Tittabawassee River Confluence (MI)*	Triclopyr acid	9.8 uM	7.0-8.0	25°C	Midland Michigan August sunlight	44.6 hours	Woodburn et al, 1993

Table 3.3
Photolysis of Triclopyr (Laboratory Studies) (continued)

Matrix	Compound	Initial Conc	pH	Temp (°C)	Other conditions	Half-life (DT_{50})	Reference
Buffered Sterile water*	Triclopyr BEE	1.0 ppm	5.0	~25°C	30 days of California sunlight	158.4 hours	EPA RED, 1998
Sterile buffered water at 35°C (Filtered Artificial sunlight = 313 Sterile buffered water	Triclopyr BEE	1.28 ppm	5.2	35°C	40° North midday sun (estimate based on laboratory studies)		McCall and Gavit, 1988
					Spring surface	16.7 hours	
					Spring 1 meter	22.0 hours	
					Summer surface	12.5 hours	
					Summer 1 meter	16.5 hours	
					Fall surface	27.6 hours	
					Fall 1 meter	36.7 hours	
					Winter surface	63.5 hours	
					Winter 1 meter	83.4 hours	
Sterile buffered water (Filtered Artificial sunlight = 313 nm)	Triclopyr BEE	1.28 ppm	5.2	35°C	Integrated intensity values for a day		McCall & Gavit, 1986
					30°N Spring	60 hours	
					30°N Summer	36 hours	
					30°N Fall	72 hours	
					30°N Winter	108 hours	

Table 3.3
Photolysis of Triclopyr (Laboratory Studies) (continued)

Matrix	Compound	Initial Conc	pH	Temp (°C)	Other conditions	Half-life (DT_{50})	Reference
Sterile buffered water (Filtered Artificial sunlight = 313 nm)	Triclopyr BEE	1.28 ppm	5.2	35°C	Integrated intensity values for a day		McCall & Gavit, 1986
					40°N Spring	84 hours	
					40°N Summer	36 hours	
					40°N Fall	120 hours	
					40°N Winter	240 hours	
Sterile buffered water (Filtered Artificial sunlight = 313 nm)	Triclopyr BEE	1.28 ppm	5.2	35°C	Integrated intensity values for a day		McCall & Gavit, 1986
					50°N Spring	108 hours	
					50°N Summer	48 hours	
					50°N Fall	180 hours	
					50°N Winter	744 hours	
Sterile buffered water (Filterd artificial sunlight = 313 nm)	TCP metabolite of triclopyr	0.99 ppm	7.0	25°C	Estimated half-lives for 40°North		Dilling et al, 1984
					Summer		
					Surface "pure" water	0.073 hours	
					1 m depth "pure" water	0.090 hours	
					1 m depth "river" water	2 .0 hours	
					Winter		
					Surface "pure" water	0.25 hours	

Table 3.3
Photolysis of Triclopyr (Laboratory Studies) (continued)

Matrix	Compound	Initial Conc	pH	Temp (°C)	Other conditions	Half-life (DT_{50})	Reference
Sterile buffered water (Unfiltered germicidal light = 254 nm)	TCP metabolite of triclopyr	80 ppm	7.0	NR	Unfiltered UV light = 254 nm, 0.5 W/ft^2 at one ft; light source 18.5 inches from surface of glass petri-dish containing 15 mL buffer	0.42 hours	Feng et al, 1998)

Note: Unless otherwise stated, all experiments utilized artificial light, usually mercury vapor lamps on an approximately 12 hours light/12 hours dark cycle.
* EPA guideline study
1 n.r. = not reported

3.4 DEGRADATION AND PERSISTENCE - SOIL

<u>Summary</u>*: When soil is contacted by triclopyr, or its main microbial degradate TCP they are not readily adsorbed since the Kd values are low on soils that contain less than 2.25% organic carbon. Except on soils that are classified as organic peaty, the Freunlich Kd-values were less than 1.0 L/Kg for triclopyr (Woodburn et al, 1988). In some cases, adsorption of triclopyr was so low that an equilibrium could not be determined. The adsorption of TCP was also low with the Freundlich* K_{ads}*-values ranging from 0.53 to 1.95 L/Kg (EPA RED, 1998). Since triclopyr and TCP are not readily adsorbed to soils, degradation by soil microbes and photolysis is likely to be rapid. The nature of degradation on soil by photolysis is currently under review by EPA but this data is not yet available to the general public (EPA RED, 1998).*

Laboratory studies indicate that triclopyr acid, the dissociated triethylamine (TEA) and hydrolyzed 2-butoxyethanol (BEOH) moieties are readily degraded in aerobic soil studies. Aerobic soil degradation of triclopyr acid ranged from 8 to 18 days in the laboratory on silt clay loam and clay loam, respectively. After 300 days of incubation 70% and 80% , respectively, of the applied ^{14}C*- triclopyr acid was mineralized to* $^{14}CO_2$*. Intermediate products prior to the formation of* $^{14}CO_2$ *consisted of 3,5,6-trichloro-2-pyridinol (TCP) and 3,5,6 tricloro-2- methoxypyridine (TMP). These products were not persistent and were seen at maximum concentrations less than 30 days after incubation was initiated. Triethylamine (TEA) and 2-butoxyethyanol (BEOH) are degradates formed by the dissociation of triclopyr TEA and hydrolysis of triclopyr BEE, respectively. These intermediate degradates are rapidly degraded under aerobic soil conditions. TEA is degraded with a half-life of 5.6 and 13.7 days on sandy loam and silt loam soils, respectively. More than 60% of the applied* ^{14}C*-TEA was mineralized to carbon dioxide in 24 and 91 days, respectively. The metabolite, BEOH, has an aerobic soil half-life of 0.375 and 0.058 days on Hanford sandy loam and Commerce silt loam, respectively. Fifty percent of BEOH is mineralized to carbon dioxide in 4 and 10 days on Hanford sandy loam and Commerce silt loam, respectively. Prior to degradation to carbon dioxide, BEOH forms an intermediate metabolite (2-butoxyacetic acid) which comprises 100% of the applied label within 24 hours of the initiation of incubation (EPA RED, 1998).*

Work in the laboratory with rice paddy soils yielded half-lives that varied considerably. However, certain trends were noted. The rate of degradation was more rapid on soils incubated at 30° than at 15°C. The rate of dissipation was about 10-fold faster (DT50 = 9 to 135 days) at 30°C than at 15°C (64 to 314 days). Rates of degradation on surface soils (DT50 = 9 to 307 days) was much greater than on soils taken from depths of about one foot (DT50 = 35 to 314 days). This phenomenon was attributed to the fact that surface soils when compared to subsurface soils had higher pH, higher organic matter content, higher microbial numbers and the presence of acclimated versus non acclimated decomposers (microbes). Although other herbicides have been shown to degrade more rapidly in water saturated soil than in soil that was not saturated with water, a strong correlation between water saturation and rate of triclopyr degradation was not seen for triclopyr acid (Johnson et al, 1995).

Large differences in the degradation rate were seen in field tests depending on the soil type and ecological system. For example, in rice paddy ecosystems, the DT50 ranged from 4 to 5 days for both flooded systems and rain-fed lowland rice paddies located in Arkansas. However, the DT50 for Northern Ontario forest soil was approximately 14 *days and the DT50 on pastureland in Oregon was approximately 80 days. The time to complete dissipation also varied dramatically depending on the soil type and ecological system. For example, in flooded rice paddies (AR), triclopyr was not detected 28 days after treatment with 0.38 lbs/acre, but in rain-fed fed low land rice paddies triclopyr persisted for more than 49 days after treatment (Johnson et al, 1995). However, pastureland continued to display high concentrations of triclopyr (~0.15 ppm) and TCP (0.04 to 0.12 ppm) for a year or more after treatment with 3.04 to 8.03 lbs a.e./acre (Norris et al, 1987). Northern Ontario forest soil treated at 2.7 lb/acre (0.55 to 0.875 ppm) continued to have residues of 0.055 to 0.035 ppm for 4 to 48 weeks after treatment (Stephenson et al, 1990).*

In most field studies, triclopyr and it metabolites were not detected at concentrations higher than 0.01 to 0.4 ppm in soil levels deeper than 0 to 6 inches. Preconditioning of the microbes, species and numbers of microbes can effect the rate at which triclopyr is metabolized. Most species were not specified in the documents that were evaluated. However a Pseudomonas *species has been documented to use the triclopyr metabolite, TCP, as its sole source of carbon-energy (Feng et al, 1997). Both TCP and TMP are the main non-volatile degradates seen in soil metabolism. Although other species of microbes have not been documented that can utilize triclopyr or its metabolites as carbon-energy sources, it seems likely that various species of microbes that can metabolize the related product (2,4-D) can also metabolize triclopyr. Some of the species that have been seen to metabolize 2,4-D include* Acaligenes eutrophus, Arthrobacter *sp*., Bordetella *sp.*, Flavobacterium *sp.*, Pseudomonas *sp.* and Xanthobacte*r sp. Unidentified mixed species of soil microorganism in laboratory aerobic soil studies have been shown to degrade triclopyr to carbon dioxide with TCP and TMP being intermediate metabolites formed prior to mineralization of the* ^{14}*C-radiolabel to carbon dioxide.*

Significant metabolites of triclopyr found on soils treated with triclopyr included TCP and TMP. Triclopyr acid, triclopyr TEA and triclopyr BEE may also be converted to photoproducts on soil. Studies concerning the photolysis of triclopyr are currently in review. Triclopyr acid is formed from the dissociation of triclopyr TEA and the hydrolysis of triclopyr BEE. However, the main aqueous photolysis products of triclopyr acid are 5-chloro-3,6-dihydroxy-2-pyridinloxyacetic acid in sterile buffer solutions and oxamic acid in natural river water. The main photolysis product of triclopyr BEE is (5/6)-chloro-3-hydroxy-s-pyridinone. Other aqueous photolysis products have also been seen at low concentrations when either triclopyr acid or triclopyr BEE are exposed to sunlight or artificial light. For a detailed discussion of photolysis products please see Section 3.3

Although only the aquatic uses of triclopyr are considered in this document, the compound is registered for terrestrial applications. Data regarding triclopyr persistence in soil are therefore required to be submitted to the EPA. This information has a relevance to accidental terrestrial overspray on lake or stream shorelines, and peripherally as an indication of possible fate on near-shore lake bottoms exposed by drought or draw-down following a triclopyr application. The degradation of triclopyr on soil also has relevance when triclopyr TEA is used to treat various broadleaf weeds and woody brush on non-submerged wetlands.

3.4.1 Half-life

Triclopyr acid, which can be formed from the dissociation of triclopyr TEA or the high pH (pH 7 to 9) hydrolysis of triclopyr BEE, is degraded rapidly on various soil types in both the laboratory and the field. Because triclopyr acid is formed rapidly from triclopyr TEA and triclopyr BEE, EPA has not required laboratory aerobic soil degradation studies on these products. However, work has been conducted on the aerobic soil degradation of the triethylamine (TEA) and 2-butoxyethyl (BEOH) moieties after they have been dissociated or hydrolyzed from triclopyr TEA and triclopyr BEE, respectively (EPA RED, 1998). The half-lives of triclopyr acid, triclopyr TEA and triclopyr BEE half-lives can vary from just a few days (DT50 = 8.0 to18 days) in laboratory aerobic soil metabolism experiments to approximately 2 weeks (DT50 = 14 days) on Northern Ontario forest soils to nearly 3 months in pastureland in Oregon (DT50 = 75 to 81 days) (Table 3.4).

Triclopyr acid is readily degraded in the laboratory on silty clay loam soil and silt loam soil under aerobic conditions. The dissociation product of triclopyr TEA (triethylamine hydrochloride) is also rapidly degraded on sandy loam soil under laboratory aerobic conditions. The hydrolysis product of triclopyr BEOH (2-butoxyethanol) is similarly degraded on Hanford sandy loam and Commerce silt loam with a half-life of less than one day. Triclopyr acid is degraded after application of ^{14}C-triclopyr acid at 1.0 ppm for an incubation period of 300 days at 25°C (EPA RED, 1998). The DT50 ranged from 8 days on silty clay loam to 18 days on silt loam. After 300 days of incubation, 80% and 70%, respectively, of the applied radioactivity was ultimately degraded to carbon dioxide. After the TEA moiety has been dissociated from triclopyr TEA, it is aerobically degraded to carbon dioxide with a DT50 of 5.6 and 13.7 days on sandy loam and silt loam, respectively. ^{14}C-TEA is ultimately degraded to $^{14}CO_2$. Sixty percent of the radiolabel is degraded to carbon dioxide after 24 days of incubation on sandy loam and 91 days of incubation on silt loam under aerobic conditions. After BEOH has been hydrolyzed from Triclopyr BEE, it is aerobically degraded to carbon dioxide with a DT50 of 0.375 and 0.058 days on Hanford sandy loam and Commerce silt loam, respectively. ^{14}C-BEOH is ultimately degraded to $^{14}CO_2$. Fifty percent of the applied ^{14}C-BEOH is degraded to carbon dioxide after 4 days of incubation on Hanford sandy loam and 10 days of incubation on Commerce silt loam under aerobic conditions.

Other laboratory work indicates that temperature, pH, higher organic matter content, higher microbial numbers and the presence of triclopyr due to previous applications may have an effect on the rate of triclopyr acid degradation. As would be predicted, the rate of degradation on soil at 30°C is significantly higher than at 15°C. For example, the rate of degradation on Crowley (AR) silt loam was 0.022 day^{-1} (DT50 = 31 days) to 0.029 day^{-1} (DT50 = 24 days) at 30°C and 0.0023 day^{-1} (DT50 = 307 days) to 0.0028 day^{-1} (DT50 = 248 days) at 15°. This data is representative of typical surface soils containing 16% to 60% water based on soil weight. Furthermore, other data in Table 3.2.4 give similar results (Johnson et al, 1995).

There is also data that indicates that soils with higher pH (pH = 6.9), higher organic matter (1.0%) and higher bacterial counts degrade triclopyr acid more rapidly than soils with lower pH (pH = 5.3), lower organic matter (0.5%) and lower bacterial counts. For example, at 30°C, Perry (AR) surface silt clay (pH = 6.9, 1.0% organic matter and high bacterial counts) had a degradation rate of 0.050 day^{-1} (DT50 = 14 days) to 0.077 day^{-1}

(DT50 = 9 days) while Perry (AR) silt clay from a depth of ~60 cm (pH = 5.3, 0.5% organic matter and low bacterial counts) had a degradation rate of 0.012 day^{-1} (DT50 = 55 days) to 0.020 day^{-1} (DT50 = 35 days). This data is representative of soils containing ~40% to 60% water based on soil weight. Furthermore, other data in Table 3.2.4 gives similar results (Johnson et al, 1995).

In a number of field studies, triclopyr applied at rates of 0.38 to 8.0 lbs a.e./acre had half-lives that varied significantly. Since triclopyr TEA, triclopyr isopropylamine and triclopyr BEE are all rapidly transformed to triclopyr acid upon contact with soil, formulation does not appear to impact the half-lives of these products.

When triclopyr BEE is applied to bare ground at rates of 6.4 lbs a.e./acre, the half-life of the combined triclopyr acid and triclopyr BEE was only 2 weeks. However when grass-covered ground was treated at the same rate, the half-life of the combined triclopyr acid and triclopyr BEE was increased to 4 to 8 weeks. Although the reason for this half-life increase was not specified, it is probable that low light levels on the grass-covered soil prevented photolysis from having an extensive impact on the degradation of triclopyr. Triclopyr was generally not seen at soil depths below 6 inches. Similar rates of degradation were seen on bare ground treated with 6.4 lbs/acre in California (DT50 = 2 weeks) and with 8.1 lbs a.e./acre in North Carolina (DT50 = 1.5 weeks) (EPA RED, 1998).

An unspecified triclopyr formulation was used to treat flooded rice paddies, rain-fed lowland rice and bare ground in Arkansas. The rate of application was 0.38 lbs a.e./acre. In rice paddy water from flooded paddies, the DT50 and DT95 were 4 and 20 days, respectively. Concentrations of triclopyr dropped below the limit of detection (LOD = 0.000001 ppm) in 28 days. In the paddy soil from flooded rice paddies the concentration of triclopyr was never detected at concentrations higher than 0.00005 ppm at soil depth of 0 to 3 or 3 to 6 inches. In rain-fed lowland rice and on treated bare ground, the DT50s and D95s were 4 to 5 days and ≥ 49 days, respectively. The longer DT95 on rain-fed lowland rice and bare ground was believed to be due to the fact that triclopyr was leached into the soil and from that time on was not subject to photolysis. Triclopyr was not extensively detected below the 3 to 6 inch soil profile in rain-fed lowland rice and bare ground applications. However, triclopyr was detected in the 3 to 6 inch soil profile of rain-fed lowland rice and bare ground in 25% to 30% of the samples (Johnson et al, 1995).

Pastureland in Oregon treated with triclopyr isopropylamine at 3.04 to 8.03 lbs a.e./ha, had DT50s on soil that ranged from 75 to 81 days. Triclopyr persisted on the 0- to 2-inch soil segment or 0- to 6-inch segment at concentrations that ranged from 0.14 to 0.18 ppm for over one year. In soil profiles below 0- to 2-inches or 0- to 6-inches the triclopyr concentration dropped to ≤0.004 ppm in one to 1.3 years (Norris et al, 1987)

In two soil types from Northern Ontario forests, the DT50 and DT95s were observed to be 14 and 28 days, respectively. The initial concentration of triclopyr in the top 6 inches of these soils ranged from 0.55 to 0.875 ppm. However, after 4 and 48 weeks of dissipation, triclopyr could still be detected in the top 6 inches at concentrations ranging from 0.035 to 0.055 ppm. Less than 3% of the triclopyr residue leached into the 6 to 12 inch soil profile and no lateral movement was observed outside the treatment area (Stephenson et al, 1990).

3.4.2 Degradation Products

Soil microorganisms have been noted to degrade triclopyr. However, only one species has been documented as being able to degrade TCP and use it as a sole source of carbon-energy. It is not clear if this species is capable of degrading parent triclopyr or using it as a sole carbon-energy source. This is a *Pseudomonas* sp., which was similar *to P. corrugata and P. marginalis*. Although identified as a separate species type, this species has not been named and has been given an American Type Culture Collection accession number of ATCC 700113 (Feng et al, 1997 and Feng et al, 1998). It is possible that other species known to degrade a similar herbicide (2,4-D) may also degrade triclopyr. Some of these species include *Acaligenes eutrophus*, *Arthrobacter* sp., *Bordetella* sp., *Flavobacteriaum* sp., *Pseudomonas* sp. and *Xanthobacter* sp. (Section 3 of 2,4-D SEIS).

It has been noted that mixed soil microorganisms from several laboratory aerobic soil metabolism experiments are capable of degrading ^{14}C-triclopyr acid to $^{14}CO_2$. The ^{14}C-TEA dissociation and the ^{14}C- BEOH hydrolysis products are also rapidly degraded to $^{14}CO_2$.

In aerobic soils, 70% to 80% of the applied triclopyr acid is degraded to carbon dioxide in 300 days. Two non-volatile degradates were formed prior to the formation of carbon dioxide. TCP (3,5,6-trichloro-2-pyridinol and TMP (3,5,6-trichloro-2-methoxypyridine) which were generally not persistent on soil and reached maximum levels of 26% and 8%, respectively. Other metabolites could potentially form from the microbial and photolytic dissipation of TCP. The microbe *Pseudomonas* sp. (ATCC700113) completely destroyed the degradates produced by photolysis with the exception of the dichlorodihydroxy-pyridines. *Pseudomonas* sp. in liquid media transformed 22.9% of the applied radiation to $^{14}CO_2$ after 2 hours of UV exposure to form photoproducts,. Only 2.3% of the applied radiation was converted to *Pseudomonas* sp. biomass and 54.2% of the radiolabel remained in the liquid media presumably as some intermediates of microbial metabolism and the original photolysis products (Feng et al, 1998). It is unclear if photolysis will be an important factor in the degradation of triclopyr and TCP on soil since many factors such as quenching, photosensitization, radical reactions, light screening, organic content, soil particle size, moisture and temperature may influence the rate of photolysis and the photolysis products that are formed (Miller and Zepp, 1983). Further discussions regarding photolysis in aqueous solutions and soil can be found in Section 3.3.

When TCP and TMP were measured in the field, it is clear that TMP is not persistent and never exceeds 0.06 ppm in any soil profile on bare ground and pastureland soil. Concentrations of TCP have been observed at 0.1 to ~0.2 ppm or higher for three-quarters of a year or longer after application of triclopyr to pasturelands. However, TCP and TMP do not normally leach below the top 6 to 12 inches of the soil profile at concentrations exceeding 0.050 ppm (Norris et al, 1987). In other field dissipation studies, triclopyr and it metabolites (TCP and TMP) have been seen to leach to considerable depths (30 to 90 cm = 1.0 to 3.0 feet) in 1 to 4 weeks, Residues in these deeper samples ranged from 0.05 to 0.120 pp. This data suggests that limited leaching of triclopyr and its degradates may occur under some conditions (EPA RED, 1998). Although field mobility does not appear to be high for either triclopyr or its metabolites, the database is quite limited and leaching cannot be ruled out. For further discussion on the leaching of triclopyr and its metabolites, see Section 3.7.

The actual pathway for the metabolism of triclopyr on soil is not known. It is known that triclopyr acid forms TCP directly when metabolized on soil, but it is unclear if TMP is formed from direct methoxylation of TCP or by some other mechanism. After TCP is formed it can be further metabolized by microbes, eventually forming carbon dioxide as an end product, or forming 2-hydroxypyridine through a photolytic reductive dechlorination and eventually undergoing ring cleavage and forming 4-oxo-4- (amino)-2-buten-1-aldehyde. Further photolysis or metabolism by *Pseudomonas* sp. can transform this product to carbon dioxide, water and ammonium ion. Alternatively, chlorine can be retained in the ring to form various dichlorodihdroxypyridines, which form chlorinated 4-carbon straight chain alkenes with triple bonded nitrogen after ring cleavage. All of these photoproducts can be degraded to carbon dioxide by *Pseudomonas* sp. except for the dichlorodihydroxypyridines which cannot be metabolized by this species (Feng et al, 1998).

3.4.3. Physical and Chemical Factors

There are several physical and chemical factors, which may influence the rate of binding and degradation of triclopyr acid and its subsequent breakdown in soil. These factors may include pH, temperature, moisture, quenching, photosensitization, radical reactions, light screening, organic content, and soil particle size (Miller and Zepp, 1983).

- **Temperature and pH**

  The rate of chemical reactions and most biological metabolic processes have been reported to double for every 10°C increase in temperature. The rate of metabolism for triclopyr on soil has been seen to more than double with a 15°C increase in temperature from 15° to 30°C. In Table 3.2.4. , the rate of triclopyr degradations has been seen to increase from about 2-fold to about 10-fold, depending on soil type. The differences in the rates of degradation is influenced by an increase in temperature and may vary with soil type, and the number and kinds of microbes present. pH, moisture content and organic content may also influence the degradation rate by making triclopyr more or less available to the resident microbes (Johnson et al, 1987). Increases in pH have been hypothesized by Johnson et al (1995) to increase the rate of degradation of triclopyr on soil. However, in light of other variables that may influence the rate of dissipation in concert with increasing pH, this hypothesis is difficult to accept. It is absolutely certain that pH can strongly affect the mobility, which in turn can affect the availability of triclopyr for degradation by photolysis or microbial metabolism. Johnson et al (1995) found that increasing pH from pH 5 to pH 7 can increase the soil mobility of triclopyr acid as indicated by a decrease in the soil water partition coefficient (Kd) by 2.5- to 7.4-fold. A similar herbicide (2,4-D) has been observed to have similar Kd values which decrease as pH is increased. The absolute Kd-values and the decrease in Kd-value with increased pH are expected to be similar for triclopyr acid ad 2,4-D acid since the pKa values are similar (2.6 for triclopyr acid and 2.8 for 2,4-D acid). Johnson believes that the rate of microbial metabolism will increase with increases in pH since triclopyr becomes less tightly bound to soil and more readily available for utilization by microbes as pH increases. Since triclopyr would be more readily leached into the soil at higher pHs, it can be conjectured that it would be less susceptible to the photolytic effects of sunlight once it has leached even to shallow depths in the soil column.

- **Soil moisture**

  Degradation on soils with normal levels of moisture has been noted to be fairly rapid (DT50 = 8 to 244 days) (EPA RED, 1998 and Johnson, et al, 1995). However, saturated soils (water tension = 0 kPa = 60% water by dry soil weight) have been noted to often degrade triclopyr acid more slowly than soils with lower moisture content (water tension = 100 kPa = 16% to 43% water by dry soil weight) (Table 3.2.4). This is in direct contrast to the data collected for 2,4-D, which showed a higher rate of degradation on water saturated soils than on soils with lower moisture content. It is not understood why these two chemically similar herbicides should behave in such directly contrary manners in relation to degradation rate and the soil moisture content**.** However, it is interesting to note that when environmental conditions are similar, triclopyr acid (DT50 = 9 to 314 days) degrades far more slowly on soil than 2,4-D BEE [(DT50 = 4 to 45 days) (Johnson et al, 1995)].

- **Organic matter and clay minerals**

  Johnson et al (1995) indicate that higher organic matter content correlates well with rate of dissipation. Although this correlation is good, soils with high organic content had other physical and biological properties, which make this hypothesis difficult to accept. Soils with high organic content also were located at the surface of the soil profile, had higher pHs, higher microbial counts and the presence of triclopyr acclimated decomposers. Since lower pHs cause greater adsorption, it is likely that clay minerals, with their high number of cation exchange sites, play a role in sorption of triclopyr through hydrogen bonding. However, Johnson et al (1995) indicated that organic matter is probably a more important factor than clay minerals in the sorption of triclopyr since sorption is inversely correlated with clay content at pH 7. Furthermore, the physical chemistry of adsorption appears to impact the rate of degradation on soils, with more rapid degradation rates occurring where the least adsorption occurs.

- **Soil microbes**

  Microbes are likely to have an impact on the rate of triclopyr degradation in soil. Only one species of bacteria has been isolated that is capable of degrading the main metabolite (TCP) and it photolysis products to carbon dioxide. This species is related to *Pseudomonas corrugata* and *Pseudomonas marginalis* and is capable of utilizing TCP as a sole carbon-energy source. However, Feng et al (1997) have indicated that this, as yet, unnamed species type is archived with the American Type Culture Collection under assession number ATCC 700113. It is not clear if this *Pseudomonas* species is also capable of using triclopyr acid as a sole carbon-energy source. Other minor degradates have been noted during aqueous photolysis experiments. They include oxalic acid, pyruvic or maleic acid and malic or 2-chlorosuccinic acid (Woodward et al, 1993). Pyruvic and maleic acid should be readily metabolized to carbon dioxide and water after entering the Krebb's Cycle in the resident microbes.

  The joint products of photolysis and microbial metabolism of triclopyr and TCP has been previously discussed. An actual pathway for the joint degradation of triclopyr by microbial metabolism and photolysis has been constructed from evidence presented in the EPA RED (1998), Feng et al (1997) and Feng et al (1998). It is known that triclopyr acid forms TCP directly when metabolized on soil but it is not clear if TMP is formed from direct methoxylation of TCP or by some other mechanism. After TCP is formed it can be further metabolized by microbes eventually forming carbon dioxide as an end product. 2-hydroxypyridine is formed through a photolytic reductive dechlorination of TCP eventually undergoing ring cleavage to form 4-oxo-4- (amino)-2-buten-1-aldehyde. This product can be transformed by further photolysis or metabolism by *Pseudomonas* sp. to carbon dioxide, water and ammonium ion. Chlorine can alternatively be retained in the ring to form various dichlorodihdroxypyridines, which in turn, form various chlorinated 4-carbon straight chain alkenes with a triple bonded nitrogen. All of these microbial metabolites and photoproducts can be degraded to carbon dioxide by *Pseudomonas* sp. except for the dichlorodihydroxypyridines, which cannot be metabolized by this species.

It has been noted that characteristics of initial lag times, and recruitment by selection of bacterial populations effective in degrading triclopyr is not an issue that needs to be addressed. There is probably little that can be done to improve the ability of soil microbes to degrade triclopyr since the ability to degrade any pesticide is genetically controlled within the bacteria. Mutations would be necessary in order for a bacterial species to utilize the pesticide as a new food source. If this occurs, bacterial populations can increase and the breakdown of the herbicide may commence. Repeat treatments in subsequent years with the same herbicide would activate the mutant bacteria and breakdown may immediately occur. The consequence of this more rapid breakdown may be that greater use rates would be necessary for control of the same weeds (Newbold, 1975). In some cases, a 14- to 28-day lag phase has been noted before more rapid dissipation of triclopyr acid occurred. This lag phase appears to be particularly obvious in subsoil that was taken from a 2-foot depth while surface soils appear to degrade triclopyr more rapidly, probably due in part to the presence of higher microbial numbers that have been acclimated by the presence of triclopyr (Johnson et al, 1995). Other data indicates that the rate of triclopyr degradation on soil is not correlated with the count of microbes that are capable of using triclopyr and/or TCP as a sole carbon-energy source. This would tend to indicate that species of microbes not capable of utilizing triclopyr as a sole carbon-energy source are also important in metabolizing triclopyr on soil. A consortium of microorganisms may be needed to achieve complete degradation of triclopyr and its metabolite TCP combined with photolytic and other non-biotic degradation mechanisms. It is possible that other species of microbes that are known to degrade a similar herbicide (2,4-D) may also degrade triclopyr. Some of these species include *Acaligenes eutrophus*, *Arthrobacter* sp., *Bordetella* sp., *Flavobacterium* sp., *Pseudomonas* sp. and *Xanthobacter* sp. (Section 3 of 2,4-D SEIS).

Table 3.4
Triclopyr Persistence in Soil

Experiment	Compound & application rate	Half-life (DT_{50})	Time to residues < 0.01ppm and Notes	Reference
Lab aerobic silty clay loam*[1]	^{14}C-Triclopyr acid at 1.0 ppm	8 days at ~25°C	n.r.[1]but 80% of applied label degraded to CO_2 in 300 days	EPA RED, 1995
Lab aerobic silt loam*[1]	^{14}C-Triclopyr acid at 1.0 ppm	18 days at ~25°C	n.r.[1]but 70% of applied label degraded to CO_2 in 300 days	EPA RED, 1995
Lab aerobic sandy loam*[1]	^{14}C –Triethylamine hydrochloride (TEA) at 5.03 ppm	5.6 days at ~25°C	n.r.[1] but 60% of applied label degraded to CO_2 in 24 days.	EPA RED, 1995
Lab aerobic silt loam*[1]	^{14}C –Triethylamine hydrochloride (TEA) at 5.03 ppm	13.7 days at ~25°C	n.r.[1] but 60% of applied label degraded to CO_2 in 91 days.	EPA RED, 1995
Lab aerobic Hanford sandy loam*[1]	^{14}C-2-butoxyethanol (BEOH) at 6.) ppm	0.375 days at ~25°C	n.r.[1] but 50% of applied label degraded to CO_2 in 4 days.	EPA RED, 1995
Lab aerobic Commerce silt loam*[1]	^{14}C-2-butoxyethanol (BEOH) at 6.) ppm	0.058 days at ~25°C	n.r.[1] but 50% of applied label degraded to CO_2 in 10 days.	EPA RED, 1995
Bare ground sandy loam soil in NC[2]	Triclopyr BEE (Garlon® 4) 8.1 lbs a.e./acre	10.6 days for combined triclopyr BEE and triclopyr acid 1.1 days for triclopyr BEE to triclopyr acid transformation	Not detected after 7 days in the 0 to 3 inch soil layer. 0.14 ppm at 4 weeks post treatment in the 6 to 12 inch soil segment and not detected at >0.02 ppm after 4 weeks. 0.03 ppm at 2 weeks in the 12 to 18 inch segment and not detected at >2 weeks.	EPA RED, 1995
Bare ground on soil in CA[2]	Triclopyr BEE (Garlon® 4) 6.4 lbs a.e./acre	2 weeks for combined triclopyr BEE and triclopyr acid	Triclopyr and its metabolites (TCP and TMP were generally not detected below 6 inches of soil depth. 0.067 ppm TCP in 0 to 6 inch segment at 28 weeks 0.05 ppm TMP in 0 to 6 inch segment at all sampling intervals	EPA RED, 1995

Table 3.4
Triclopyr Persistence in Soil (continued)

Experiment	Compound & application rate	Half-life (DT_{50})	Time to residues < 0.01ppm and Notes	Reference
Ground covered with native short grasses in CA[2]	Triclopyr BEE (Garlon® 4) 6.4 lbs a.e./acre	4 to 8 weeks for combined triclopyr BEE and triclopyr acid.	Triclopyr and its metabolites (TCP and TMP were generally not detected below 6 inches of soil depth.	EPA RED, 1995
Crowley (AR) silt loam[1];0-4 cm (surface) soils with pH = 6.9, 0.8% organic matter, 19% clay and 19 cmole/Kg	Triclopyr acid at 5.0 ppm	At 15° and 60% water by mass DT50 = 307 days At 15° and 16% water by mass DT50 = 248 days At 30° and 60% water by mass DT50 = 31 days At 30° and 16% water by mass DT50 = 24 days	n.r.[3] No lag phase	Johnson et al, 1995
Crowley (AR) silt clay loam[1]; 58-62 cm (deep soil) soils with pH = 5.0, 0.7% organic matter, 37% clay and 26 cmole/Kg	Triclopyr acid at 5.0 ppm	At 15° and 60% water by mass DT50 = 314 days At 15° and 24% water by mass DT50 = 272 days At 30° and 60% water by mass DT50 = 108 days At 30° and 24% water by mass DT50 = 135 days	n.r.[3] A lag phase of 14 to 28 days occurs prior to rapid dissipation	Johnson et al, 1995

Table 3.4
Triclopyr Persistence in Soil (continued)

Experiment	Compound & application rate	Half-life (DT_{50})	Time to residues < 0.01ppm and Notes	Reference
Perry (AR) silt clay[1]; 0-4 cm (surface soil) soils with pH = 6.9, 1.0% organic matter, 50% clay and 43 cmole/Kg	Triclopyr acid at 5.0 ppm	At 15° and 60% water by mass DT50 = 99 days At 15° and 38% water by mass DT50 = 64 days At 30° and 60% water by mass DT50 = 9 days At 30° and 38% water by mass DT50 = 14 days	n.r.[3] No lag phase	Johnson et al, 1995
Perry (AR) silt clay[1]; 58-62 cm (deep soil) soils with pH = 5.3, 0.5% organic matter, 56% clay and 48 cmole/Kg	Triclopyr acid At 5.0 ppm	At 15° and 60% water by mass DT50 = 285 days At 15° and 43% water by mass DT50 = 209 days At 30° and 60% water by mass DT50 = 35 days At 30° and 43% water by mass DT50 = 55 days	n.r.[3] A lag phase of 14 to 28 days occurs prior to rapid dissipation	Johnson et al, 1995
Paddy Soil & Paddy Water (AR)[2] In flooded rice paddy with 3 to 17 cm depth	Triclopyr formulation not specifed 0.38lbs a.i./acre	Paddy water DT50 = 4 days DT95 = 20 days Paddy soil n.r.	28 days not detected at 0.001 ppb Not detected at soil depths of 0 to 3 or 3 to 6 inches at concentrations higher than 0.050 ppb	Johnson et al 1995
Paddy soil[2] in rain-fed lowland rice (AR)	Triclopyr formulation not specified 0.38lbs a.i./acre	System Paddy soil and water combined DT50 = 4 days DT95 = ≥49 days	≥49 days Protected from hydrolysis since triclopyr has been transported into the ground by precipitation and irrigation	Johnson et al 1995

Table 3.4
Triclopyr Persistence in Soil (continued)

Experiment	Compound & application rate	Half-life (DT_{50})	Time to residues < 0.01ppm and Notes	Reference
Bareground[2] (AR)	Triclopyr formulation not specified 0.38lbs	System soil and water combined DT50 = 5 days DT95 = ≥49 days	≥49 days Protected from hydrolysis since triclopyr has been transported into the ground by precipitation and irrigation	Johnson et al 1995
Pastureland in Coquille (OR)[2]; silt clay loam with 2-5% organic matter and a 34% slope	Triclopyr isoproplyamine salt 3.04lbs a.e./acre Triclopyr isopropylamine salt	DT50 = 75 days	Triclopyr 0.18 ppm in 0-2 inch soil after 1 year aging. Triclopyr 0. 01ppm in 2-6 inch soil after 1 year aging Triclopyr <0. 01ppm in 6-12 inch soil after 0.75 year aging	Norris et al, 1987
Pastureland in Coquille (OR)[2]; silt clay loam with 2-5% organic matte and a 34% slope	Triclopyr isopropylamine salt 3.04lbs a.e./acre Applied May 24	DT50 = 75 days	TMP 0.05 ppm in 0-2 inch soil after 1 year aging. TMP 0.01 ppm in 2-6 inch soil after 1 year aging TMP <0. 01ppm in 6-12 inch soil after 0.5 year aging	Norris et al, 1987
Pastureland in Corvallis (OR)[2]; silty clay loam with 3.8% organic matte and a 15% slope	Triclopyr isopropylamine salt 8.03 lbs a.e./acre Applied June 24	DT50 = 81 days	Triclopyr 0.14 ppm in 0-6 inch soil after 1.3 years aging. Triclopyr 0. 04 ppm in 6 –12 inch soil after 1.3 year aging Triclopyr 0. 01ppm in 12-18 inch soil after 1.3 year aging	Norris et al, 1987

Table 3.4
Triclopyr Persistence in Soil (continued)

Experiment	Compound & application rate	Half-life (DT_{50})	Time to residues < 0.01ppm and Notes	Reference
Pastureland in Corvallis (OR)[2]; silty clay loam with 3.8% organic matte and a 15% slope	Triclopyr isopropylamine salt 8.03 lbs a.e./acre Applied June 24	DT50 = 81 days	TCP 0.04 ppm in 0-6 inch soil after 1.3 years aging. TCP <0. 01 ppm in 6 –12 inch soil after 1.3 year aging TCP <0.01 ppm in 12-18 inch soil after 0.3 year aging	Norris et al, 1987
Pastureland in Corvallis (OR)[2]; silty clay loam with 3.8% organic matte and a 15% slope	Triclopyr isopropylamine salt 8.03 lbs a.e./acre Applied June 24	DT50 = 81 days	TMP <0.01 ppm in 0-6 inch soil after 1.3years aging. TMP <0.01 ppm in 6 –12 inch soil after 1.3 year aging TMP 0.01 ppm in 12-18 inch soil after 1.3 years aging	Norris et al, 1987
Northern Ontario forest soil – organic layer[2]; sand soil with pH = 4.5 to 5.0, 33.8% organic mater	Triclopyr BEE (Garlon® 4) 2.7lbs/acre on June 18	DT50 = 14 days DT95 = 28 days	Triclopyr in top 6 inches of soil 0.055 ppm for 4 to 48 weeks after treatment. Initial concentration was ~0.55 ppm. Less than 3% of the applied residues leached into the 6 to 12 inch soil level. No lateral movement of triclopyr was seen.	Stephenson et al 1990

Table 3.4
Triclopyr Persistence in Soil (continued)

Experiment	Compound & application rate	Half-life (DT_{50})	Time to residues < 0.01ppm and Notes	Reference
Northern Ontario forest soil – organic layer[2]; clay soil with pH = 5.0 to 5.4, 74.2% organic mater	Triclopyr BEE (Garlon® 4) 2.7lbs/acre on June 18	DT50 = 14 days DT95 = 28 days	Triclopyr in top six inches of 0.055 ppm for 4 to 48 weeks after treatment. Initial concentrations was ~0.875 ppm Less than 3% of the applied residues leached into the 6 to 12 inch soil profile. No lateral movement of triclopyr was seen.	Stephenson et al 1990
Ten Corn soils from Iowa and Illinois	TCP metabolite 5 ppm	DT50 = 8 to 12 days for 4 most active soil DT50 ≥ 14 days for 6 less active soils	n.r.[3] but 62 to 80 % of the applied label was degraded to CO_2 in 14 days	Racke et al, 1988
Ten Corn soils from Iowa and Illinois	TCP metabolite 50 ppm	n.r. but ≥ 14 days	n.r.[3] but only 4% of the applied label was degraded to CO_2 in 14 days	Racke et al, 1988

1	Laboratory experiment
2	Field experiment
3	n.r. = not reported
*	EPA guideline study

3.5 DEGRADATION AND PERSISTENCE - AQUATIC SYSTEMS

Summary: *The action of microorganisms associated with a water body and its sediment layer can apparently degrade triclopyr to TCP and possibly TMP. Persistence of triclopyr in water bodies may also be controlled by photolysis and dissipation from a water body due to the joint actions of advection and dispersion. After treatment of a laboratory microcosm containing only water and sediment, the half-life varied depending on the test substance (triclopyr TEA or triclopyr BEE) and the incubation conditions (aerobic or anaerobic). Under aerobic aquatic conditions, triclopyr TEA had an extrapolated half-life of 142 days. In the 30 days that the test system was incubated, less than 5% of the applied label was converted to TCP. Under anaerobic aquatic conditions triclopyr BEE was transformed to triclopyr acid in 5 hours. The resident triclopyr acid subsequently had a DT20 of about 365 days and an extrapolated half-life of 1,300 days. After 365 days, 25% of the applied label was degraded to TCP from triclopyr acid. Based on these observations, triclopyr may have a very long half-life in field if it is associated with anaerobic sediment (EPA RED, 1998 and Laskowski and Bidlack, 1984 in Getsinger, 2000).*

The degradation of the triclopyr TEA dissociation product (^{14}C-triethylaminne hydrochloride = ^{14}C-TEA) and the triclopyr BEE hydrolysis product (^{14}C-2-butoxyehanol =^{14}C-BEOH) were also studied. Under laboratory aerobic aquatic conditions, TEA applied at 1.33 ppm had a short water residence time. However, while very little degradation of TEA occurred during the first 14 days, the DT50 was only 18 days; at this time more than 60% of the applied ^{14}C-TEA was evolved as $^{14}CO_2$ and 25% of the radioactivity was bound to the sediment. This bacterial degradation can result in the virtual elimination of oxygen from the test system for up to 7 days. ^{14}C-BEOH is also degraded rapidly under aerobic aquatic conditions with a first order half-life of 0.6 to 3.4 days. The intermediate metabolite was seen to be ^{14}C-2-butoxyacetic acid (53.9% after 10 days) and had a half-life of ~1.0 days. This hydrolysis product (BEOH) of triclopyr BEE is ultimately mineralized to $^{14}CO_2$ (69% after 10 days) and 9.9% of the applied label was bound to the sediment. A decrease in dissolved oxygen levels was not discussed for the metabolism of this hydrolysis product of triclopyr BEE (EPA RED, 1998).

When ^{14}C-TEA was applied at 1.36 ppm to anaerobic microcosms, the calculated half-life was 2 years. TEA was evenly distributed between the water and sediment extracts. Less than 1% of the applied label formed volatile products ($^{14}CO_2$) and 10% to 19% of the applied label was bound to the sediment. However, the hydrolysis product (^{14}C-BEOH) of triclopyr BEE was degraded rapidly under anaerobic conditions with a half-life of only 1.4 days. The 2-butoxyacetic acid intermediate metabolite was formed rapidly and had a half-life of 73 days which was much longer than those seen under aerobic conditions. The ultimate degradation product of ^{14}C-BEOH was carbon dioxide with 57.4% $^{14}CO_2$ formed after 193 days of incubation; ^{14}C-residues bound to the sediment reached a maximum of 9.9% of the applied label after 29 days of incubation (EPA RED, 1998).

The rate of degradation in laboratory aerobic and anaerobic aquatic studies is primarily governed by the action of microbes. Although few microbes have been identified which are known to degrade triclopyr to carbon dioxide, a Pseudomonas *species has been positively identified that degrades the intermediate metabolite (TCP) to carbon dioxide (Feng et al, 1998 and Feng et al, 1997). It is likely that a consortium of microorganisms*

are needed to achieve complete degradation of triclopyr and its metabolite (TCP) in the aquatic environment, water treatment plants or sewage plants.

A number of bacteria that are known to degrade the chemically related 2-4-D may also degrade triclopyr. These include Acaligenes eutrophus, Arthrobacter *sp.,* Bordetella *sp.,* Flavobacterium *sp.,* Pseudomonas *sp. and* Xanthobacter *sp. (Section 3 of 2,4-D SEIS).*

The half-lives of triclopyr TEA and triclopyr BEE in field situations varied from <1.0 days to 7.5 days (Ritter and Peacock, 2000 and Solomon et al, 1988). The rate of dissipation could be affected by the product applied, time of year, cloud cover, temperature and the latitude of the water body, amount the light transmittance and the amount of advection and dispersion and the size of the treatment area. Other properties of the chemical under aquatic aerobic or anaerobic conditions could also effect the rate of dissipation. These properties include solubility, vapor pressure, octanol/water partition coefficient, adsorption coefficient and photolysis rate. Additional properties of the water body could also effect the rate of degradation and dissipation including the amount of organic matter in the sediment, sediment thickness, cation and anion exchange capacities, bacterial count and bacterial type in the benthic sediment, biomass and bulk density. It is not entirely clear how these and other properties effect the aqueous dissipation of triclopyr. For a detailed discussion of how these parameters are used in an EXAMS II model, please see Ritter and Peacock (2000).

Triclopyr is dissipated rapidly from the water column and is not adsorbed on sediment for very long periods of time. In an experiment designed to mimic the worst case in the field, ponds in California, Missouri and Texas were treated with triclopyr at concentrations of 2.5 ppm a.e. These duplicate pond mesocosms were fairly small with a square area of not more than ~30,000 ft^2. The water half-lives for triclopyr and its metabolites (TCP and TMP) was up to 7.5, 10.0 and 7.7 days, respectively. The sediment half-lives of triclopyr and TCP were similar to those seen in the water column with DT50s as high as 4.6 and 7.0 days, respectively. Since triclopyr does not significantly adsorb to the sediment, it is expected that the degradation rates in water and sediment would be similar (Petty et al, 1998). The concentration of triclopyr in the water decreased below the MCLG (0.5 ppm a.e.) in approximately 3 weeks but was still seen at low concentrations (0.001 ppm a.e.) after 84 weeks of dissipation. Concentrations of triclopyr in the sediment reached a maximum of 0.68 ppm a.e. 3 days after application and dissipated to below detectable levels (<0.003 ppm a.e.) after 28 days. However, the concentrations of TCP and TMP in sediment were always fairly low and never exceeded 0.128 ppm and <0.002 ppm, respectively. However, it took 84 days for TCP to dissipate below the limit of detection on sediment (<0.003 ppm). The half-life of triclopyr, TCP and TMP in the water column at Columbia, Missouri and Lewisville, Texas were similar to those seen in Elk Grove, California. The sediment half-lives of TCP and TMP at the Columbia or Lewisville sites were similar to those values found at the Elk Grove site. It also took approximately 3 weeks for triclopyr to dissipate to concentrations below the MCLG (0.5 ppm a.e.) at the Columbia and Lewisville sites. It took 4 to 6 weeks for TCP and TMP to dissipate from the water column at Columbia and Lewisville sties. The concentration of triclopyr in sediment reaches a maximum of 0.173 and 0.264 ppm a.e. at 1 week and 1 day after application at the Columbia and Lewisville sites, respectively, and it took 4 and 12 weeks, respectively, to dissipate to concentration below 0.003 ppm a.e. The metabolite TMP was not detected in sediment at any time during the study. The water quality at these sites did not seem to be affected by the use of triclopyr TEA. Generally speaking, the dissolved oxygen content, pH and conductivity did not vary *significantly between treated and untreated ponds. However, the water quality in all ponds change as the year progresses in a diurnal pattern typical of that expected for small constructed impoundments for the regions studied (Petty et al, 1998). Light transmission was quenched by 50% to 90% in the top 0.5 to 0.8 meters of the water column, which leads to the conclusion that photolysis may play a limited roll in the degradation of triclopyr and TCP.*

In flooded impounded rice fields (AR and LA), treated at rates of 0.375 lbs a.e./acre, the triclopyr half-lives in the water column was similar to those seen in pond situations. After the first treatment, the water half-lives were <8 days (range 1.8 to 7.6 days) and the soil half-lives were less than 12 days (range 2.9 to 11.7 days). Concentrations of triclopyr in water dissipate to levels of 0.006 to 0.015 ppm in 28 days. On soils at the end of the flood period, triclopyr dissipated to concentrations of <0.01 to 0.026 ppm (EPA RED, 1998).

Numerous physical and chemical factors can effect the persistence and fate of triclopyr in the aquatic environment. Temperature influences the rate of both chemical and biological processes. Since triclopyr acid is not readily hydrolyzed at typical environmental temperatures, it appears unlikely that temperature will influence the degradation of triclopyr by hydrolysis. Generally, the adsorption by various soil/sediment types is extremely limited with Freundlich K_{ads} *values for triclopyr acid ranging from 0.165 to 0.975 L/Kg (Woodburn et al, 1988) and the Freundlich* K_{ads} *values for TCP ranging from 0.18 to 1.95 L/Kg (Woodburn et al, 1988 and EPA RED, 1998). The concentration of triclopyr in sediments of hard water, high pH ponds like those discussed here would be at a minimum since it has been shown that increases in pH decreases the adsorption of triclopyr acid to a minimum (Johnson et al, 1995). However, since the effects of pH on adsorption can be expected to be minimal in the normal environmental range (pH 6.5 to 8.5), metabolism of free triclopyr by aquatic (water and sediment) microbes should remain high. Most importantly the degradation of triclopyr by microflora will be inhibited at low water temperatures. Johnson et al (1995) has shown that the rate of degradation of triclopyr acid on soil/water slurries and damp soil increases with an increase in temperature with the rate (30°C) being 2.0- to 11-fold more rapid than that at lower temperatures (15°C). It seems reasonable to expect that within a very broad range of normal environmental temperatures (~5 to ~45°C), the rate of microbial degradation will increase by 2-fold for every 10°C increase in temperature that occurs. Water pH does not appear to play a significant role in the hydrolysis of triclopyr acid or triclopyr TEA. Triclopyr BEE is rapidly converted to triclopyr acid at all reasonable pHs, particularly in the presence of soil or sediment (EPA RED, 1998 and McCall et al, 1998). The amount of oxygen dissolved in a water body should have a direct effect on the speed of triclopyr degradation. However, in most field studies dissolved oxygen is not an issue when triclopyr TEA or triclopyr BEE is used to control aquatic weeds. In almost all cases, the dissolved oxygen content will follow a diel pattern. In many cases, eutrophic and even mesotrophic lakes are more likely to support large populations of microorganisms that can metabolize unabsorbed triclopyr more rapidly than lakes with lower nutrient levels. On the other hand, if carbon sources are not abundant, competition for the carbon in triclopyr can favor growth of the microbiota that can utilize triclopyr exclusively. It seems likely that a consortium of microorganisms may be needed to achieve complete degradation of triclopyr and its TCP metabolite (Feng et al, 1998).*

Probably the most important physical process affecting triclopyr persistence in larger water bodies is transport of treated water away from the treatment area and replacement with untreated water through lateral circulation or vertical movement of water. For example, the larger the lake, the more wind blowing across the lake surface, the more water exchange through inlet and outlet streams or rivers, the more likely it is that triclopyr residues will be rapidly dispersed and diluted to below detection limits. In small lakes, detectable concentrations of triclopyr may be carried a significant distance down an outlet stream if the flow is sufficient and degradation is slow. Vertical dispersion is the dominant mechanism of dilution in whole-treated lakes, while a combination of vertical and horizontal water movement contributes to dispersion and dilution in lakes treated over only a part of their surface.

Lakes and rivers have been seen to degrade triclopyr TEA at very rapid rates. For example, at Banks Lake, Washington treated at 27 to 30 lbs a.e./acre, the DT50 was observed to be <1.0 day at both the top and bottom of the water column. Triclopyr and TCP were not detected in the water column or the sediment during the course of the study. The rapid dissipation of triclopyr from this lake was believed to be due to sustained high winds (10 to 15 mph) that occurred immediately after treatment.

Other lakes had triclopyr water column half-lives that varied from 0.5 days to approximately 5 days. For example, at Lake Seminole, Georgia, the triclopyr half- life that varied from 0.5 days to 3.4 days and the water dissipation time for triclopyr ranged from less than 8 days to dissipate to <0.01 ppm a.e. to more than 21 days to dissipate to 0.03 ppm a.e. In both cases the initial concentration of triclopyr acid ranged around 3.0 ppm when the nominal application rate to a 10-acre area was 2.5 ppm. The differences in the treatment site influenced dissipation rate. More rapid dissipation occurred at the site that was open on three sides and was less than 1.0 Km from the main channel and experienced extensive currents and wind generated mixing. Slower dissipation occurred at the site that was protected on two sides, was 2-3 Km from the main channel and experienced limited current and wind generated mixing. TCP concentrations were not seen in the water column after 1-day post-treatment. In the sediment, concentrations of triclopyr and TCP were not seen at or above the limit of detection, which was 0.1 ppm a.e. for triclopyr and 0.025 ppm for TCP. Concentrations of triclopyr found 300 feet outside the plot were similar to those found within the treatment plots. However, concentrations of triclopyr 5,000 feet outside the plot could not be detected.

Another set of treatments at Lake Seminole indicated that within 1 day of treatment at 1.0 ppm on a 1 acre plot, the concentration of triclopyr inside the plot and 165 feet outside the plot was similar(~0.025 ppm. At a higher treatment rate (2.5 ppm a.e.), The concentration of triclopyr found inside this plot was 0.145 ppm a.e. but 165-feet outside this plot the concentration (0.020 ppm a.e.) was only ~one-tenth of the concentrations inside the plot. In 7 days the concentration in the treatment zone fell below the limit of detection (<0.01 ppm) in the water column at the site treated with 1.0 ppm a.e. and 0.015 ppm at the site treated with 2.5 ppm a.e. At both treatment sites, the concentration of triclopyr in the sediment dissipated to <0.1 ppm a.e. within 14 days of application.

Other lakes also demonstrated fairly rapid dissipation of triclopyr and its metabolite of toxicological concern (TCP). With water column half-lives were typically near 4.5 days at Lake Minnetonka, Minnesota (Petty et al, 1998 and Getsinger et al, 2000) and a bog lake in Ontario (Solomon et al, 1988). When measured, the DT50 of TCP in the water column at Lake Minnetonka could be as high as 4 to 8 days. The dissipation half-life for *triclopyr and TCP in sediment is typically around 5 to 6 and 10 days, respectively. Concentrations of triclopyr typically dissipate to levels that are below the MCLG (0.5 ppm a.e.) in 7 to 14 days after application of 2.5 ppm triclopyr and dissipate to very low levels (0.002 to 0.008 ppm) in about 42 days. The concentration of TCP is always low in the water column (maximum concentrations never exceeding 0.024 ppm) and dissipated to around the limit of quantitation (0.00015 to 0.0002 ppm) in 42 days. The concentration of TMP in the water column had a maximum concentration of 0.004 ppm on the third day after application. Outside the treatment area (100 to 800 meters), triclopyr is only seen at concentrations that exceed the MCLG (0.5 ppm a.e.) at 5 days after treatment in an area that is 100 meters downstream. Concentrations of triclopyr, TCP and TMP are not persistent with concentrations dropping below < 0.01 ppm in 42 days. The persistence of triclopyr and it metabolites in water and sediment were shorter in Phelps Bay (open at both end)s than in Carsons Bay (open at only one end). Twelve acre bog lakes located in Ontario exhibited similar half-lives for triclopyr when the treatment rate was 0.012 and 0.12 ppm, respectively, and the persistence time was about 42 days in the water column and 100 days in the sediment (Solomon et al, 1988).*

Wetlands near Moses Lake, Washington were treated with 0.53 gallons formulation per acre, resulted in residue concentrations in adjacent water bodies that ranged between 0.06 to 0.43 ppm formulation equivalence immediately after treatment, and the highest concentration detected during the seven days of monitoring was 0.833 ppm (Gardner and Grue, 1996).

Treatment of the Pend Oreille River (Washington) at concentrations of 1.7 ppm (in an embayment) and 2.5 ppm (in a riverine section) resulted in triclopyr half-lives of 57.3 hours and 19.4 hours, respectively. Concentrations of triclopyr dissipated to <0.01 ppm in 14 and 7 days, respectively. Concentrations less than the MCLG (0.5 ppm) occurred at 500 feet for the treated embayments and 2,200 feet for the treated riverine sites. It is noteworthy that dissipation occurred more rapidly in open riverine areas than in embayments (Getsinger et al, 1997).

This data indicates that concentrations of triclopyr immediately after treatment are not likely to have adverse impact on fish or invertebrates since the concentration likely to impact the environment adversely [110 ppm formulation equivalence (32 ppm a.e.)] is much higher than the 0.1 to 10 ppm formulation equivalence of triclopyr (0.032 to 3.2 ppm a.e.) that is typically found in the environment (Gardner and Grue, 1996).

Modeling results based on the work presented above indicate that the set back distance from water intake valves can vary with application rate and purpose (Ritter and Peacock, 2000). However, in large treatment areas (14 ha = 34.6 acres), a treatment of 2.5 ppm to control submerged weeds would require a set back distance of 600 meters (~2,000 feet) to prevent exposure at concentrations that exceed the MCLG (0.5 ppm). In similar sized treatment areas, treatment at 1.48 ppm to control emerged plant species would require a set back distance of 380 meters (~1,300 feet). Smaller treatment areas and lower treatment concentrations require less setback distance. The label should be consulted to determine the setback distance for a particular treatment scenario.

The disappearance of triclopyr from a lake or other natural water body is influenced by a number of factors as discussed earlier in Section 3.1.4.3. Various water chemistry conditions and physical conditions (such as temperature, pH adsorption to the sediment, dissolved oxygen content, effects of photolysis and the extent of water currents and dilution) can have very pronounced effects on triclopyr persistence. This section reviews the triclopyr disappearance times reported for natural water bodies and for artificial laboratory microcosm and mesocosm studies (small and medium scale simulations) and also looks at the reported factors that can influence such times.

3.5.1 Half-life and Disappearance Time

Table 3.5 summarizes the half-lives of triclopyr and its degradates (TCP and TMP) as reported in research papers, as well as the time to non-detection or very low levels as specified in the Table 3.5. A half-life is the time required for an herbicide to reach half of its initial concentration determined immediately following application. Concentrations of triclopyr and its degradates may also be reported at various times during their dissipation. Depending on the type of study and the data collected, a half-life may be mathematically calculated using several analyses over time, or may be interpolated from tabular data or figures given in a cited paper as was sometimes necessary in this review.

Time to disappearance is the time necessary for an herbicide's concentration to drop below the lower limit of analytical detection (LOD). This value varies with the analyte (triclopyr, TCP and TMP) and the matrix. The LOD for triclopyr, TCP and TMP is usually ~0.00004, ~0.0001 and ~0.00003 ppm, respectively in water and ~0.003, ~0.003 and ~0.002 ppm on sediment. Because of the variety of analytical techniques used (instrumental chemical analysis, bioassay or ELISA) the LOD varied over time.

Half-life values are important for estimating persistence, but can be misleading if the herbicide remains in the environment at significant concentrations after the half-life time. Times to disappearance are useful tools for predicting impacts on biota and wildlife, particularly when used with calculated or estimated half-lives (Ritter and Peacock, 2000). The persistence of triclopyr and its degradates varies widely depending on the conditions of the system being tested. Therefore, it is not surprising that a wide range of half-life and disappearance times have been reported in the literature.

A large portion of the non-published scientific studies were conducted to support the registration of triclopyr products. These studies describe laboratory microcosm/flask and aquarium studies as opposed to natural water body studies. Laboratory studies allow more control over water chemistry and temperature as well as the determination of degradates formed if desired. They are useful for isolating the effect of specific factors on triclopyr persistence. On the other hand, studies in natural lakes and ponds subject the herbicide to 1) temperature and pH variations, 2) a greater variety of microorganisms, 3) a greater water:sediment surface ratio (thus affecting adsorption), and 4) dilution and movement throughout the lake. There are few reported data concerning the persistence of triclopyr and its degradates in sediment; most of the water/sediment studies report separate half-lives for the water and the sediment phases. However, in laboratory experimental microcosms, the system aerobic aquatic half-life for triclopyr acid was 142 days. The system anaerobic aquatic half-life for triclopyr BEE was 1,300 days, which is expected for anaerobic aquatic systems at the bottom of a deep water column where the oxygen has been depleted (EPA RED, 1998 and Laskowski and Bidlack, 1984 in Getsinger et al, 2000). Most of the applied triclopyr appears to be associated with the flood waters under anaerobic aquatic conditions and concentrations of triclopyr bound to the sediment will probably be fairly low due to the low soil/water adsorption coefficient (EPA RED, 1998, Woodburn et al, 1988).

Two EPA guideline aquatic metabolism studies were conducted at 25°C using ^{14}C-labeled triclopyr acid and ^{14}C-labeled triclopyr BEE. In the 30-day aerobic study (EPA RED, 1995), less than 5% of triclopyr acid was degraded to 3,5,6 -tcrichloro-2-pyridionl (TCP). This study was judged to be inadequate to support registration since the formation and degradation of TCP was not adequately described. An anaerobic aquatic study conduced with triclopyr BEE was also judged to be inadequate since only 20% to 25% of the triclopyr acid produced by the hydrolysis of triclopyr BEE was converted to TCP during the 365-day study duration. The characterization of the sediments was not reported beyond the soil type (silty clay soil and silt loam soil for the aerobic aquatic study and sandy loam for the anaerobic studies). However, supplemental information concerning the long half-life of triclopyr and the fact that TCP is formed can serve as supplemental information needed in risk assessments.

The dissociation product (TEA) of triclopyr TEA and the hydrolysis product (BEOH) of triclopyr BEE are of environmental concern (EPA RED, 1998). Under aerobic conditions TEA has a DT95 of 18 days when 60% of the applied label has been converted to $^{14}CO_2$ and 25% of the applied labels in bound to the sediment. The laboratory aerobic microbial metabolism of the degradate TEA produces anaerobic conditions for up to 7 days after application of the degradate TEA (EPA RED, 1998). BEOH is also degraded to under 2-hydroxyacetic acid under aerobic conditions with a half-life of 0.6 to 3.4 days. This intermediate metabolite, 2-butoxyacetic acid, is further degraded with a half- life of 1 day. By the end of 10 days 69% of the applied label was degraded to $^{14}CO_2$ and only ~10% of the applied label remained bound to the sediment. Under anaerobic conditions, the degradate TEA is much more persistent with a half-life of 2 years. No significant degradation was seen during the 6-month course of the study. TEA was evenly distributed between the water and the sediment and 10% to 19% of the label was bound to the sediment. Under anaerobic conditions the degraded BEOH was rapidly converted to the intermediate 2-butoxyacetic acid (DT50 = 1.4 days). However, the intermediate was slow to degrade with a half-life of 73 days. During the 193 days of the study only 57.4% of the applied ^{14}C-BEOH label was converted to $^{14}CO_2$.

Several authors have conducted field studies with triclopyr and determined its levels in water and sediment at several different times after treatment. For example, Petty et al (1998) conducted small pond studies in California, Missouri and Texas designed to show the worst case dissipation in triclopyr TEA treated ponds. Two ponds at each site with a three foot depth were treated at concentrations of 2.5 ppm a.e.). At the Elkgrove, CA site, the sediment was characterized as a clay loam and had organic matter levels ranging from 0.8% to 2.5% and a neutral to slightly acid pH. At the Columbia, MO site, the sediment was a silty clay loam with an organic matter content of 2.0% to 3.4% and a slightly alkaline pH. At the Lewisville, TX site, the sediment was a sandy clay loam or sand with an organic matter content of 2.1% to 3.8% and a slightly alkaline. The sorptive capacity of these sediments appeared to be fairly low. Although samples of water were taken from two separate depths (one-third and two-thirds of the total depth) it is apparent that the samples were combined for analysis of triclopyr, TCP and TMP. Samples of sediment were taken from the top 5 cm of the pond bottom with a post hole digger. It is not clear why the water column dissipation rates were different at the different sites but the water half-lives for triclopyr range from as high as 6.9 to 7.5 days at the California site to 5.9 to 6.1 days at the Missouri sites. The Texas site had water column dissipation half-lives of 6.3 to 6.5 days. The water column dissipation half-lives for the triclopyr degradates (TCP and TMP) were ~5 days at the California site, 4 to 8 days at the Missouri site and 6 to10 days at the Texas site. In general, the dissipation rates for triclopyr and TCP were similar in both the sediment and the water. This was anticipated for compounds that do not readily bind to sediment. The sediment half-lives for triclopyr were ~4 days, ~3 days and ~5 days for the California, Missouri and Texas sites, respectively. The sediment half-lives for TCP were 4 to 6, 6 to 7 and 7 to 13 days for the California, Missouri and Texas sites, respectively. It takes 3 to 4 weeks for the triclopyr concentration to fall below the MCLG (0.5 ppm) in water at the California site but only 2 to 3 weeks at the Missouri site and 3 weeks at the Texas site. It can take up to 42 days for triclopyr to dissipate to insignificant levels (<0.01 ppm a.e.), and after 84 days of dissipation, the triclopyr concentrations in the water column fall to between 0.006 and 0.009 ppm a.e. The EPA considers TCP to be a toxicologically significant metabolite, while TMP is not considered to have toxicological significance. It takes approximately 28 days for the TCP levels in the water column to drop to ~0.001 ppm at all 3 sites and after 42 days of dissipation the TCP levels have dropped to <0.00015 ppm at all sites. The levels of TMP in water were always low, averaging less than 0.007 ppm at all dissipation times tested. In sediment, concentrations of triclopyr and TCP are always low with concentrations of triclopyr falling below the limit of detection (<0.003 ppm a.e.) within 42, 42 and 84 days for the California, Missouri and Texas sites, respectively. No TMP was detected in sediment (<0.002 ppm) at any of the experimental sites. Since it can take up to 3 to 4 weeks for the triclopyr levels to fall below the MCLG (0.5 ppm a.e.), the three week potable water use restriction required for pond water in the Garlon® 3A label is warranted.

In real field situations, the dissipation rate can vary dramatically. Water column half-lives for triclopyr in lakes and rivers have ranged from less than a day at Banks Lake, WA (EPA RED, 1998) and Lake Seminole, GA (Green et al, 1989) to nearly 5 days in an embayment at Lake Minnetonka, MN (Petty et al, 1998, and Getsinger et al 2000). Water column half-lives for the main metabolite (TCP) were generally not reported but it ranged around 4 to 8 days at Lake Minnetonka. In these lake situations, the sediment half-lives of triclopyr and TCP were not generally documented, but the half-lives of triclopyr in the sediment ranged from around 5 or 6 days at Lake Minnetonka, and the sediment half lives of TCP were approximately 11 days in this water body. The reasons for rapid or slow dissipation are well documented. Rapid dissipation is associated with high winds occurring shortly after the treatment of a water body. Rapid dissipation is also associated with unprotected situations (not in an embayment and not protected by landmasses), the water flow rate and nearness of the main hydraulic channel in slow moving rivers and “lakes”.

Dissipation in Banks Lake was very rapid. When this lake was treated at 27 to 30 lbs a.e./acre, the DT50 was <1.0 day at both the top and bottom of the water column. Triclopyr and TCP were not detected in the water column or sediment during the course of the study. The rapid dissipation of triclopyr from this lake was believed to be due to sustained high winds (10 to 15 mph) that occurred immediately after treatment (EPA RED, 1998). This is expected since sustained high winds can rapidly mix the water column causing both horizontal and vertical dispersion.

In Lake Seminole, GA, triclopyr has been used to control 1 acre plots (1.5meter depth) of Eurasian water milfoil at rates of 1.0 ppm a.e. and 2.5 ppm and 10 acre plots of containing primarily Eurasian watermilfoil and hydrilla. In the 1 acre plots treated with 1.0 or 2.5 ppm a.e. triclopyr, the water column half-life of triclopyr was 4.5 and 1.9 days, respectively. It was unclear why the rate of dissipation was longer in the plot treated at the lower rate. After 1 day of dissipation, the concentration of triclopyr inside the treatment plots were 0.025 ppm and 0.15 ppm a.e. for the 1.0 and 2.5 ppm treatment pots, respectively. The concentration of triclopyr after 1 day of dissipation at the top, middle and bottom of the water column for each treatment plot was approximately equal to the mean concentration which indicates that vertical dispersion is rapid. At 165 feet downstream from the treatment plots the concentration of triclopyr in the 1.0 ppm plot was 0.023 ppm a.e. and the concentration of triclopyr in the 2.5 ppm plot was 0.020 ppm a.e. It is unclear why extensive lateral dispersion occurred in the low rate plot but not in the high rate plot. However, the rapid dissipation and low concentration of triclopyr were believed to be due to extensive sorption of triclopyr by Eurasian water milfoil and dissipation by water currents (Getsinger and Westerdahl, 1984). At all time intervals, the concentration of triclopyr in the sediment was <0.1 ppm a.e. for both treatment plots, which indicates that adsorption of triclopyr to the sediment can be expected to be minimal under this treatment scenario. The time to dissipation to water concentrations that are below the MCLG (0.5 ppm a.e.) is less than one day at both sites and the time to dissipation below the LOD (0.01 ppm a.e.) was 7 and 14 days at the sites treated with 1.0 and 2.5 ppm, respectively.

Subsequent experiments in Lake Seminole yielded even shorter water column half-lives for triclopyr. The water column half-lives for triclopyr ranged from 0.5 days to 3.4 days. When the half-lives at different depths were measured, these values were similar to the mean half-life for a given treatment scenario. Triclopyr in the water column dropped to nearly non-detectable levels (<0.01 to 0.03 ppm) in 8 to 21 days. The amount of TCP in the water column was below the limit of detection after one day of dissipation. Water concentrations of triclopyr 300 feet outside the test plot are similar to those found within the treatment plots. However, concentration of triclopyr was not detected 5,000 feet outside the plot. In the top 4 inches of sediment, the concentration of triclopyr dropped to below the limit of detection (<0.10 ppm a.e.) after 1 day of dissipation and the metabolite, TCP was never detected. More rapid dissipation occurred at the site that was open on 3 sides and less than 1.0 Km from the main channel and experience extensive currents and wind generated mixing. Slower dissipation occurred at the site that was protected on 2 sides, was 2-3 Km from the main channel and experienced limited currents and wind generated mixing.

Other lakes also demonstrated fairly rapid dissipation of triclopyr and its metabolite TCP. The water column half-lives varied from around 4 to 5 days at Lake Minnetonka, MN (Petty et al, 1998 and Getsinger et al, 2000) and a bog lake in Ontario (Solomon et al, 1988). The DT50 of TCP in the water column at Lake Minnetonka was as high as 4 to 8 days. The dissipation half-life for triclopyr and TCP in sediment is typically around 5 to 6 and 10 days at Lake Minnetonka. Concentrations of triclopyr typically dissipate to levels below the MCLG (0.5 ppm a.e.) in 7 to 14 days after application of 2.5 ppm triclopyr and dissipate to very low levels (0.002 to 0.008 ppm) in about 42 days. The concentration of TCP is always low in the water column with maximum concentrations never exceeding 0.024 and dissipating to near the limit of quantitation (0.00015 to 0.0002 ppm) in 42 days. The concentration of TMP in the water column was at a maximum concentration of 0.004 ppm on the third day after application. Outside the treatment area (100 to 1600 meters), triclopyr and its TCP metabolite are not seen at significant concentrations (≤0.006 ppm) after 42 days of dissipation. However, concentrations higher than the MCLG (0.5 ppm a.e.) were found 100 meters outside the treatment area within 5 days of application at the Phelps Bay site but not at the Carson Bay site. At other setback distances (400 to 1,600 meters) no concentrations of triclopyr exceeding the MCLG (0.5 ppm a.e.) were found. Concentrations of triclopyr, TCP and TMP are not persistent in the sediment with concentrations dropping < 0.01 ppm in 42 days. The persistence of triclopyr and its metabolites in water and sediment were shorter in Phelps Bay (open at both ends) than in Carsons Bay (open at only one end). Twelve acre bog lakes located in Ontario exhibited similar half-lives for triclopyr when the treatment rate were 0.012 and 0.12 ppm, respectively, and the persistence time was about 42 days in the water column and 100 days in the sediment. (Solomon et al, 1988).

When wetlands near Moses Lake, WA were treated with 0.53 gallons formulation per acre, the residue concentrations in adjacent water bodies ranged between 0.06 to 0.43 ppm formulation equivalence immediately after treatment and the highest concentration detected during the 7 days of monitoring was 0.833 ppm formulation equivalence (Gardner and Grue, 1996). These concentrations are predicted to be safe for the aquatic environment since the typical LC50 (110 ppm formulation equivalence) for aquatic organisms is much higher than triclopyr concentration values (0.1 to 10 ppm formulation equivalence) typically found in the environment. Concentration values presented in this paragraph are probably in formulation equivalence, although the paper by Gardner and Grue is not entirely clear on this matter.

Treatment of the Pend Oreille River (WA) at concentrations of 1.7 ppm (in an embayment) and 2.5 ppm (in a riverine section) resulted in triclopyr half-lives of 57.3 hours and 19.4 hours, respectively. Concentrations of triclopyr dissipated to <0.01 ppm in 14 and 7 days, respectively. Concentrations less than the MCLG (0.5 ppm) occur at 500 feet (150 meters) for treated embayments and 2,200 feet (675 meters) for the treated riverine sites. Dissipation occurred more rapidly in open riverine areas than in embayments (Getsinger et al, 1997).

Modeling results based on the work presented here indicate that the set back distance from water intake valves can vary with application rate (Ritter and Peacock, 2000). However, in large treatment areas (14 hectare = 35 acres), a treatment of 2.5 ppm to control submerged weeds would require a set back distance of 600 meters (~2,000 feet) to prevent exposure at concentrations that exceed the MCLG (0.5 ppm). In similar sized treatment areas, treatment at 1.48 ppm to control emerged plant species would require a set back distance of 380 meters (~1,300 feet). Smaller treatment areas and lower treatment concentrations require less setback distance. These modeled set back distances accurately reflect the set back distances at Lake Seminole, and Pend Oreille River sites seen when the concentration of triclopyr was less than the MCLG (0.5 ppm). However, the Lake Minnetonka site appeared to require a setback distance (400 meters) that was much less than the value predicted by the model.

When triclopyr BEE (Garlon® 4) is applied to riparian environments in Ontario, high concentrations were seen only when the treatment was applied by direct over-spray to a boreal forest stream. When applications of 3.4 lbs a.e./acre were applied to a boreal forest stream by direct over-spray, the concentration of triclopyr BEE ranged from 0.23 to 0.35 ppm. These concentrations dissipated to below 0.05 ppm within 3 to 8 hours after application. At all sampling times, the concentration of triclopyr acid was seen to be less than to approximately equal to the triclopyr BEE concentrations after a direct over-spray. When only the riparian shoreline was sprayed and no direct over-sprays occurred, the concentration did not exceed ~0.2 ppm with a maximum concentration typically found 2 hours after application. The concentrations of triclopyr BEE dropped below 0.05 ppm approximately 3 to 4 hours after the last application. No TCP residues were detected in the water at any time during the monitoring period, and no triclopyr BEE, triclopyr acid or TCP were detected in the water column more than 72 hours after the last application. Runoff events due to rainfall cause a rise in the total triclopyr concentrations with a maximum of 0.09 ppm occurring 6 hour after the rainfall peak; concentration of triclopyr decreased to <0.02 ppm within 20 hours of the rainfall peak. In order for rainfall to carry triclopyr into an adjacent stream, it typically must occur within a few days of the last application. Triclopyr BEE, triclopyr acid and TCP were generally not found in the sediments of this treated boreal stream. However, 30 days after treatment, triclopyr acid was found in the sediment at 0.2 ppm. This was the only detection of triclopyr residues in the sediment (Thompson and Staznik, 1991). Although bioaccumulation of triclopyr BEE plus triclopyr acid appeared to be relatively high in both plants (8 to 225 ppm) and fish (43 ppm), environmental dissipation and regulatory restrictions were considered to be sufficient so that significant impacts to non-target aquatic organisms would not be expected. Dissipation of triclopyr from fish tissue was observed to be very rapid with less than 0.08 ppm triclopyr remaining in fish tissue 3 days after the maximum residues were observed. Even in plant tissue concentrations of triclopyr were 10-fold lower when plants were taken from outside the treatment area than when plants were taken from the treatment area.

3.5.3 Physical and Chemical Factors

Few studies designed to ascertain the effects of various water and sediment parameters on the persistence of triclopyr in aquatic systems are available. Most were conducted under a controlled set of conditions, or were field studies under uncontrolled conditions. In most studies with variable conditions, it was not possible to separate out the effects of the specific variables discussed below. Although there is some dispute amongst researchers on the relative importance of photolysis, microbial degradation and adsorption to plants, it is apparent that these factors play a significant role in the dissipation of triclopyr under certain conditions. Other factors including pH and adsorption to soil/sediment probably do not play a significant role in the dissipation of triclopyr under natural conditions since hydrolysis and sorption are minimal except at extremes where neutral to high pH will decrease the amount of sorption to a minimum (Kd = 0.08 to 0.23 at pH 7) and will increase the rate of hydrolysis of triclopyr BEE to triclopyr acid (hydrolysis half-life = 84, 8.7 and 0.3 days at pH 5, 7 and 9, respectively). The most important mechanisms of dissipation from the water column appear to be microbial degradation and photolysis, and some authors believe that photolysis is not important when the water depth is more than 15 cm (Petty et al, 1998). In aquatic systems (lakes and rivers) where there is even a slow downstream flow, the effects of advection and dispersion may be important. For example, Getsinger et al (1997) and Petty et al (1998) found that the dissipation half-life for triclopyr matches fairly well with the water turnover half-life. Although advection and dispersion appear to be important based on data from treatment of the Pend Oreille River (Getsinger et al, 1997), Lake Seminole (Green et al, 1989) and Lake Minnetonka (Getsinger et al, 2000 and Petty et al, 1998), it is unlikely that these processes would be important in small ponds that have little or no inflow or outflow of water.

- **Temperature**

  Temperature has a pronounced effect on the rate of chemical reactions and metabolic processes. In the case of triclopyr, where biological degradation predominates, temperatures outside the optimum range for triclopyr degradation are likely to result in decreased microbial degradation. A consortium of microflora is likely to degrade triclopyr to TCP and eventually to CO_2 so temperatures at which microbial degradation of triclopyr and TCP can be expected to be broad. Only one study was done that shows that a water/soil slurry or moist soil degrade triclopyr at more rapid rates at 30°C than at 15° (Table 3.4) (Johnson, 1995). Triclopyr has half-lives that are 2- to11-fold shorter at 30° than at 15°C. Details of this increase in microbial degradation rate due to the increase in temperature are discussed in Section 3.4. Triclopyr BEE is also hydrolyzed to triclopyr acid at a more rapid rate at high temperatures than at low temperatures and this process works in concert with increasing pH. For example, the half-lives for this conversion at 15°C, 25°C and 35°C and pH 9 are 0.5 hours, 0.15 hours and 0.06 hours, respectively. At a pH of 5 the half-lives for this conversion are 208, 83 and 25.9 hours, respectively. Greater details and discussion of this temperature effect can be found in Table 3.2 and in Section 3.2 (McCall et al, 1988). Water temperatures high enough to inhibit triclopyr metabolism in bacteria and fungi are unlikely to occur in Washington lakes. In this moderate climate, the most likely effect would be caused by cooler temperatures at night and at greater lake depths. Because of the high specific heat of water it is a good thermal insulator, the temperature of average size lakes does not vary much from night to day at the surface and even less at greater depths. Water temperatures of perhaps 10° to 21°C may be expected in medium size lakes during the times when aquatic weed control is a concern. Smaller or shallow lakes may be expected to be warmer than larger lakes.

In deeper lakes a thermocline can form during summer months wherein there is a sharp boundary between the warmer surface water and cold deeper water. A thermocline could increase triclopyr persistence in two ways 1). As there is little exchange of water across the thermocline, there is less water volume to dilute the herbicide, particularly in lakes treated over a large percentage of their surface. 2) Any triclopyr that penetrates the thermocline encounters a colder environment where degradation by microbes is slowed. These potential thermocline effects were discussed by Getsinger et al (2000) citing Laskowski and Bidlack (1984), but the increased half-lives (DT50 = 3.5 years) observed in artificial deep water sediments were attributed more to low dissolved oxygen levels that occur in deeper waters and associated sediments than to decreases in temperature.

Laboratory studies, typically conducted at 20°C to 25°C (68°F to 77°F), may yield half-lives that are somewhat longer than studies in ponds or lakes. In addition, the latitude of the lake with varying temperature regimes, make comparisons difficult. For example, EPA (EPA RED, 1998) noted that the half-lives for triclopyr in laboratory aquatic microcosms were quite long. Under aerobic and anaerobic aquatic conditions at 25°, the half-lives for triclopyr acid or triclopyr BEE were extrapolated to be 142 and 1,300 days, respectively. However, under field conditions where average temperatures could be much higher or lower than 25°C, photolysis, advection and dispersion can play important roles, the rate of dissipation could be less than 1 to approximately 5 days in some lakes and rivers (Getsinger et al 2000; Petty et al, 1998; Green et al, 1989; Getsinger and Westerdahl, 1984; Getsinger et al, 1997 and Solomon et al, 1988) to 2.2 to 7.5 days in small ponds and rice paddies. The rate of dissipation may be markedly influenced by temperature, particularly in ponds and rice paddies where temperatures may be very high. For example, the temperature in ponds located in Elk Grove, CA, Columbia, MO or Lewisville, TX can reach 31°C, ~35°C and ~31°C, respectively. These temperatures can be maintained for up to several days and may be part of the reason for the rapid dissipation of triclopyr in these small ponds (Petty et al, 1998). The temperatures in these ponds were fairly uniform from the top to the bottom. The temperature in the sediment and lack of significant adsorption to the sediment resulted in half-lives and dissipation of triclopyr and its metabolites (TCP and TMP) that are similar in both the water column and the sediment.

- **PH**

Alkalinity and acidity appear to have no significant impact on the degradation of triclopyr acid or triclopyr TEA. Within a very large range (pH 5 and pH 9) hydrolysis has no effect on the degradation of the inorganic salts of triclopyr (EPA, RED, 1995) (Table 3.2.2). However, triclopyr BEE is certainly rapidly transformed to triclopyr acid and 2-butoxyethanol (BEOH) when the water pH is higher than 7.0. At temperatures of 25° and pH 5, the half-life for this hydrolysis ranges from 84 to about 2,000 hours; at pH 7, this hydrolysis half-life varies from 8.7 to about 200 hours; at pH 9, this hydrolysis half-life varies 0.15 to about 7.2 hours. An important factor, which influences the rate of hydrolysis is the buffer strength (EPA, RED, 1998; Szeto, 1993 and McCall et al, 1988). The rate of hydrolysis was catalyzed by phosphate buffer concentrations of 0.2 Molar. This catalytic effect was much lower at buffer concentrations of 0.01 M. The catalytic effect of buffers in increasing the rate of hydrolysis for triclopyr BEE to triclopyr acid has some effect down to buffer concentrations of 0.001 Molar but below this buffer strength, this rate of hydrolysis does not decrease significantly (Szeto et al, 1993).

The pH can also influence the dissipation of triclopyr by changing the soil water partition coefficient. At low pHs (5), the partition coefficient typically ranges from 0.51 to 0.61, at pH 7, the partition coefficient typically ranges from 0.08 to 0.23. The rate of degradation on soil is generally more rapid when the partition coefficient is lower. Therefore, if all other soil parameters are equal, one would expect the rate of degradation for triclopyr to be higher on high pH soils; that is, the half-life of triclopyr should be shorter on high pH soils (Johnson et al, 1995).

In most natural waters, pH values are typically 6 to 9 (Reid, 1961, Goldman and Horne, 1983), aside from unusual lakes such as bog lakes, alkaline lakes, or those subject to acid rain, few of which are found in Washington State. The higher values are generally found during spring and summer, when more vigorous algal growth use large amounts of dissolved CO_2, driving the pH toward alkalinity through the carbonate/bicarbonate cycle. The more eutrophic (nutrient rich) a lake is, the larger the chance of enhanced algal growth and a higher pH.

- **Aerobic state**

The amount of oxygen dissolved in the water can have an effect on triclopyr persistence since degradation is largely the result of the action of aerobic microflora, which require oxygen, although it is apparent that triclopyr can also be slowly degraded anaerobically by some aquatic microbes. Dissolved oxygen (DO) levels are typically 6 ppm to 10 ppm in well-mixed natural water bodies, though levels outside of that range are not unknown. The colder a water body, the higher the saturation value, or the maximum amount of DO that it can hold.

Dissolved oxygen (DO) primarily enters the water from the atmosphere and from the respiration of algae and submerged plants. Fish and microflora consume dissolved oxygen from the water column and water entrained with the sediments. Zooplankton and bottom-dwelling organisms such as aquatic insects, crustaceans and gastropods also consume dissolved oxygen. Plants also consume limited amounts of oxygen in their "dark cycle" metabolism at night. Decay of vegetation and other organic materials, primarily on the lake bottom, also consumes significant oxygen. If a thermocline forms, water circulation is impaired and the water below the thermocline will become anaerobic if all of the dissolved oxygen is consumed.

Laboratory microcosm work indicates that triclopyr is slowly degraded under anaerobic conditions, such as those that exist in deeper waters and associated sediments. In that study, triclopyr degraded to TCP with a half-life of 1,300 days (Laskowski and Bidlack, 1984 in Getsinger et al, 2000). Other microcosm studies with the dissociation product (triethylamine hydrochloride = TEA) of triclopyr TEA indicate that when TEA is degraded oxidatively, the dissolved oxygen levels may decrease substantially shortly after treatment, and anaerobic conditions (DOC = 2 ppm) can exist for at least 1 to 7 days (EPA, 1998).

Although the dissolved oxygen content was seen to be high in the field (often saturated) during daylight hours, it dropped to nearly zero in the nighttime hours. This phenomenon occurred at both treated and untreated sites. Dissolved oxygen content and other water quality parameters like hardness, conductivity and pH also changed with the course of the season and did not seem to be related to the treatment scenarios. The DOC usually dropped or remained unchanged and the hardness conductivity and pH increased as the season progressed. In one case (Lake Minnetonka), the DOC levels in the bottom waters increased for the first few weeks after treatment and then returned to normal levels at 5 to 6 weeks post treatment. This increase in DOC was caused by removing Eurasian watermilfoil, which prior to treatment, had been removing oxygen from the water column due to natural metabolic function and preventing re-oxygenation by restricting the flow of water in this lake. As natural native plants like *Potamogeton zosteriformis* increased in the water column, the dissolved oxygen content at the bottom of the lake again decreased to low levels. The pH decreased slightly and the conductance was noted to increase slightly shortly after treatment of the lake sites with triclopyr. These changes in water quality after treatment with triclopyr were believed to be due to an increase or decrease in photosynthesis and an increase or decrease in water circulation within the treatment area. Changes in water quality did not significantly impact the numbers or diversity of the aquatic animal biota and in most cases the water quality was not markedly different in control and treated ponds. Discussion of this lack of change in water quality after treatment with triclopyr can be found in Petty et al (1998), Green et al (1989), Green and Westerdahl, (1984). Although the water quality and particularly the dissolved oxygen content was observed to be mostly unaffected in small plot treatments (1 to 10 acres), it was conjectured that treatment of larger areas of the whole water body could potentially cause adverse impact on water quality, particularly the DOC.

- **Trophic state**

The trophic state of a natural water body may exert an indirect influence on triclopyr persistence just as it often does with other herbicides. Because eutrophic (high nutrient concentrations) and high-end mesotrophic lakes are likely to have larger macrophyte populations, they are more likely to be included in an aquatic weed control problem. In eutrophic lakes, with a high level of nutrients, microflora populations can be expected to be greater than in mesotrophic or oligotrophic lakes (medium to low nutrient concentrations). Therefore, a larger population of microflora, many of which may degrade triclopyr, can be expected to be present and persistence would be expected to be shorter. Conversely, when a large pool of carbon is available from decaying plant and animal matter, triclopyr and other herbicides may not be utilized by microorganisms as readily as in lower-trophic state lakes. This appears to be confirmed by the observation that Lake Seminole, which is a eutrophic lake, degrades triclopyr at a much more rapid rate than Lake Minnetonka, which is an oligotrophic lake. Nevertheless, mesotrophic and especially eutrophic water bodies usually have a higher population of algae that can substantially contribute to the restoration of DO following an aquatic plant-kill from a triclopyr or other herbicide application as discussed above, and can thus help speed degradation by aerobic microflora. Species of microflora, which have potential to degrade triclopyr are those that are known to degrade the related herbicide 2,4-D [(i.e. *Acaligenes eutrophus*, *Arthrobacter* sp., *Bordetella* sp., *Flavobacterium* sp., *Pseudomonas* sp. and *Xanthobacter* sp. (Section 3 of 2,4-D SEIS)]. However, this is just a hypothesis, and except for *a Pseudomonas* species that is known to degrade the triclopyr metabolite TCP, no rigorous scientific evidence exists that these bacteria degrade triclopyr acid or its metabolites. However, it seems likely that a consortium of microorganisms may be needed to achieve a complete degradation in of triclopyr and TCP in both natural water bodies and at water and sewage treatment plants (Feng et al, 1998).

Based on the fact that algal blooms do not seem to occur with great frequency after treatment with triclopyr TEA, it seems unlikely that extensive nutrient release occurs after treatment. It has been noted that after treatment with triclopyr TEA green algae and diatoms eventually dominate the water column while the numbers of blue-green algae decreased. It should be noted that green algae increased in the untreated ponds at levels similar to those found in untreated ponds. It was unclear if triclopyr had any direct or indirect impact on the growth of algae in treated water bodies. However, healthy and diverse phytoplankton populations were generally seen in treated water bodies and it is likely the moderate and stable summer temperatures had a greater impact on this than the treatment with triclopyr TEA (Petty et al, 1998). These healthy and diverse phytoplankton populations had an impact on the aquatic invertebrate populations, which also maintain healthy and diverse populations in triclopyr-treated water bodies (Petty et al, 1997 and Green and Westerdahl, 1984). It seems reasonable to expect that high nutrient levels can occur after the treatment of a water body with triclopyr TEA or another herbicide. This is particularly likely when a large area of a water body or the whole water body is treated with triclopyr or another herbicide. High nutrient levels usually give rise to a dense population of algae and various macrophytes as well as phytoplankton and benthic organisms. In any lake, there is a continuous process of decay of a large number of dead organisms occurring, particularly on the lake bottom. In a eutrophic lake, a proportionately larger amount of decaying organisms can be expected. The first stages of this decay are generally aerobic, using dissolved oxygen. If conditions such as poor water circulation, the formation of a thermocline, or a population crash of a dense species occurs, the bottom of the lake (and possibly shallower depths) can become anaerobic. The inhibiting effects of low DO on triclopyr-degrading microorganisms then may become a significant factor in the persistence of the compound. However, to date this effect of low DO at the bottom of a triclopyr treated water was only hypothesized from the results on laboratory anaerobic aquatic microcosm studies where the half-life has been seen to be 1,300 days (Laskowski and Bidlack, 1984 in Getsinger et al, 2000).

- **Adsorption to sediment**

  Adsorption and uptake of triclopyr by aquatic macrophytes and algae is addressed in Section 4 of this document. In general, adsorption to all soils and sediments tends to be low. The adsorption of triclopyr is believed to have little impact on the dissipation of triclopyr. The concentrations of triclopyr (1.0 to 2.0 ppm a.e. in pond water for 2 weeks) and TCP (0.003 to 0.012 ppm in pond water for 2 weeks) are typically much lower (10-fold lower) on sediment than in water. The other common metabolite (TMP) is at low concentrations in pond water (<0.004 ppm) (Petty et al, 1998). If a target species (Eurasian watermilfoil) and a non-target species like *Potamogeton Zosteriformis* are both present in a treated lake the target species will bioaccumulate triclopyr at concentrations approximately 10-fold above the concentration (~2.0 ppm a.e.) typically found in water 3 days after treatment. However, there did not appear to be a tendency for the non-target plants to bioaccumulate triclopyr in their tissues (Getsinger et al, 2000). Adsorption of triclopyr by a variety of sediments was found to be extremely low and reversible with soil adsorption coefficients typically much lower than 1.0 L/Kg (typical range 0.012 to 1.7 L/Kg) (EPA RED, 1998 and Johnson et al, 1995). However, sediments with high organic matter (peaty soils with 84% organic matter) may extensively adsorb triclopyr (Kd = 13 to 20 L/Kg) (Jotcham et al, 1989). Obenshain et al (1997) has indicated that adsorption of triclopyr is so low that it cannot normally be measured and that after it is adsorbed triclopyr is almost entirely desorbed within 24 hours. It is apparent that triclopyr, due to its very low adsorption, is available for microbial degradation and that the rate of this degradation is more rapid on soils with low soil/water adsorption coefficients (Johnson et al, 1995). The adsorption and desorption coefficients of the main metabolite (TCP) are also low and generally reversible with the soil adsorption coefficient typically being less than 1.0 L/Kg [(typical range 0.53 to 1.95 L/Kg for adsorption and 0.18 to 0.58 L/Kg desorption (EPA RED, 1998 and Woodburn et al, 1988)]. The poor adsorption of TCP to soil would also indicate that it is biologically available for microorganisms to degrade.

- **Transport and dilution**

  Important and obvious physical processes affecting triclopyr concentration are photolysis and microbial degradation. However, an even more important factor is the amount of triclopyr lost from the mixing of water due to its advection (velocity) or dispersion (vertical mixing and lateral mixing) within the water column. This factor can be substantial in slow-moving lakes and rives like Lake Seminole, Lake Minnetonka and the Pend Oreille River. The half-lives of triclopyr and the metabolite TCP in Lake Minnetonka (DT50 = 3.7 and 4.7 days for triclopyr and 4.2 and 7.9 days for TCP) are similar to the half-lives demonstrated for water turnover demonstrated by the use of Rhodamine WT dye (DT50 = 3.9 and 6.3 days) in Phelps Bay and Carsons Bay, respectively. The Rhodamine WT dye was also detected at down stream sampling sites 100 to 400 meters at times that were similar to those when triclopyr was detected. For example, dye was first detected 100 to 400 meters from the sampling site from 6 to 12 hours after application while triclopyr and TCP were detected at these sampling sites from 3 to 12 hours after application. The dye was not detected 800 to 1,600 meters downstream until 2 weeks after application. However, triclopyr and TCP at low levels (~0.0001 to 0.0007 ppm) were typically detected within 1 week of application at these fairly distant sites (Petty et al, 1998). No explanation was given for the more rapid downstream movement of triclopyr and TCP relative to the dye. However, the correlation between the concentration of the dye versus triclopyr and TCP concentrations was very high within the Phelps Bay and Carsons Bay treatment sites (r = 0.86 to 0.99).

Similar observations were made in the Pend Oreille River. The half-lives in the Pend Oreille River (DT50 = 19 hours and 52 hours) are similar to the half-lives demonstrated for water turnover demonstrated by the use of Rhodamine WT dye (DT50 = 20 and 52 hours) in riverine and cove treatment areas, respectively. The results from this treatment indicate a high correlation between the concentrations of the dye versus the concentration of triclopyr in riverine and cove treatment areas of the Pend Oreille River [r = 0.88 and 0.93 (Getsinger et al, 1997)].

The data cited above indicate that transport and dilution of triclopyr by downstream flow may be the most important dissipation mechanism in slowly moving lentic and lotic systems. Also supporting this observation is that systems that are more open and/or nearer to the main channel dissipated triclopyr and its metabolite TCP at rates faster than systems that are protected or distant from the main channel. For example, at Lake Seminole, the dissipation rate at a site open on 3 sides and only 1.0 Km from the main channel had a triclopyr half-life of 0.5 days while a site protected by land masses on 2 sides and 2 to 3 Km from the main channel had a triclopyr half-life of 3.4 days (Green et al, 1989 and Woodburn et al, 1993). Similarly, a cove site (Phelps Bay) in Lake Minnetonka that was open at both ends had triclopyr and TCP half-lives of 3.7 and 4.2 days, respectively, while a site (Carsons Bay) that was open at only one end had a triclopyr and TCP half-lives of 4.7 and 7.9 days, respectively. Similar results were obtained in the Pend Oreille River. In riverine areas with relatively rapid flows, the triclopyr half-life has only 19 hours, but in coves where the flow rate was practically non-existent, the triclopyr half-life was increased to 52 hours (Getsinger et al, 1997).

Although transport and dilution play important roles in the dissipation of triclopyr and its main metabolites, pond systems, where little or no inward or outward flow occurs, also have very short triclopyr, TCP and TMP half-lives. For example, the half-lives of triclopyr, TCP and TMP at the Elk Grove, CA ponds were seen to be as high as 7.5, 4.5 and 7.7 days, respectively. Similar half-lives were seen in Columbia, MO ponds (DT50 = 6.1, 5.9 and 4.8 days, respectively) and Lewisville, TX ponds [DT50 = 6.5, 10.0 and 6.5 days, respectively (Getsinger et al, 2000 and Petty et al, 1998)].

In cases where triclopyr, TCP and/or TMP were monitored in sediment, the rate of dissipation and half-lives were typically similar in both sediments and water despite sediment concentrations of 5- to 10-fold less in sediment than in water. This indicates that triclopyr and its degradates are not truly adsorbed to the sediment prior to aging and even after aging only a small amount of the triclopyr or TCP may be associated with interstitial water. Therefore, triclopyr and TCP are not extensively protected from the degradative activity of microbes. The rate of dissipation appeared to be rapid in all field situations. However, the rate of dissipation of triclopyr and its degradates could be as much as 2-fold faster or slower on sediment than in the water column.

- **Type of formulation**

Currently only the Garlon® 3A, and Renovate® labels (44.4% triclopyr TEA salt; 31.8% triclopyr acid equivalents = 3 lbs a.e./gallons as a liquid formulation) is used for a number of terrestrial, wetland and aquatic applications. Garlon® 4 (67% triclopyr BEE; 48% triclopyr acid equivalence) liquid formulation is used for a number of terrestrial applications but is not registered for aquatic use. Although there are other formulations of triclopyr, none of these are likely to be used for the control of aquatic weeds or wetland weeds. The use of liquid formulations usually results in higher initial water residues than with granular formulations since the entire application is present immediately in the water column. Sediment concentrations can be expected to be lower with liquid formulations since the chemical is injected in the upper water column, relatively far from the sediment surface, and must be carried to the sediment by water currents or dispersion.

Although granular formulations of triclopyr are currently not used for the control of aquatic and wetland weeds, granular formulations of aquatic herbicides are discussed here since major competitors of triclopyr including Aquathol® (Potassium Endothall), Hydrothol® 191 [(Endothall mono(N,N-dimethylamine salt)], Navigate® (2,4-D BEE) and Aqua-Kleen® (2,4-D BEE) are marketed in a granular form. Granular formulation can be expected to give higher initial sediment concentrations and lower water concentrations. As granular endothall and 2,4-D BEE are released from the granules over time, sediment concentrations will likely persist, albeit at low levels, for a longer period than with a liquid formulation and water concentrations are likely to be very low or non-detectable. Since the bottom waters in deeper lakes and shoreline areas are frequently colder than surface and mid-water depths, the higher sediment concentrations that granular formulations may produce are more likely to persist for a longer period in colder and oxygen-poor water due to inhibition or slowing of microbial metabolism of the chemical.

Except in very shallow littoral areas, herbicide in liquid formulations can be expected to have less direct impact on deep-water or sediment-dwelling organisms than comparable granular formulations because of generally lower sediment concentrations and shorter persistence resulting from use of the liquid form.

Because triclopyr TEA is extremely water soluble, it dissociated to triclopyr acid in which form it is readily degraded by photolysis and the action of microorganisms. Triclopyr acid is also readily dissipated from sediment since it is easily desorbed to the water column and may also be degraded by microbial metabolism. Triclopyr acid in the water column is also readily dissipated through advective and dispersive downstream, lateral and subsurface movement of water within the water column.

For a detailed discussion of the effects of granules of Aqua-Kleen®, Navigate®, Aqauthol® or Hydrothol® 191, please see Sections 3 for 2,4-D and Endothall. The function of granular formulations is discussed in great detail in these sections.

Table 3.5
Triclopyr Persistence in Aquatic System

System	Formulation	Initial application rate	Half-life (DT$_{50}$)	Time to disappearance[1]	Comments	Reference
Laboratory Aerobic Aquatic microcosm Silty clay soil:water*	^{14}C Triclopyr TEA	n.r.[2]	System[3] DT50 = 142 days	n.r.[2] >30 days. <5% of applied ^{14}C-label was transformed to TCP. n.s.d.[4]	System was only incubated for 30 days. <5% of applied ^{14}C-label was transformed to TCP	EPA RED, 1998 & Woodburn & Cranor in Getsinger et al 2000
Laboratory Aerobic Aquatic microcosm*	^{14}C-Triethylamine hydrochloride (^{14}C-TEA)	1.33 ppm	System[3] No significant degradation in 14 days DT95[5] = 18 days	n.r.[2] but by 18 days 60% of applied ^{14}C-label degraded to $^{14}CO_2$ and only 5% of applied label remained as ^{14}C-TEA. 25% of the applied label was bound to sediment	Dissolve oxygen content decreased from ~6.6 ppm to <2 ppm at 1 to 7 days after treatment	EPA RED, 1998
Laboratory Aerobic Aquatic microcosm*	^{14}C-2-butoxyethanol (BEOH)	4.03 ppm on volume of water 42.7 ppm on weight of sediment	System[3] DT50 = 0.6 to 3.4 days DT50 of 2-butoxyacetic acid DT50 = 1 day	n.r.[2] but by 3 days 53.9% of the applied label was oxidized to 2-butoxyacetic acid. By 10 days, 69% of the applied label degraded to $^{14}CO_2$ and 9.9% of applied label bound to sediment.	System was only incubated for 10 days	EPA RED, 1998
Laboratory Anaerobic Aquatic microcosm*	^{14}C-Triclopyr BEE but degrades to ^{14}C-triclopyr acid in 0.20 days (5 hours)	n.r.[2]	System[3] DT20 = ~365 days Extrapolated DT50 = 1300 days	n.r.[2] but by 365 days, about 80% of the applied label remained as unchanged triclopyr acid. After 365 days, approximately 25% of the applied label was degraded to TCP from triclopyr acid. n.s.d.[4]	Triclopyr BEE was rapidly (5 hours) and totally (hydrolyzed to triclopyr acid). System was incubated for only 5 days. After 365 days the majority of the remaining radioactivity was associated with the floodwater.	EPA RED, 1998 & Laskowski & Bidlack, 1984 in Getsinger et al 2000

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT$_{50}$)	Time to disappearance[1]	Comments	Reference
Laboratory Anaerobic Aquatic microcosm*	^{14}C-triethylamine hydrochloride (^{14}C-TEA HCL)	1.36 ppm	System[3]: Extrapolated DT50 = 2 years	n.r.[2] but only 1% of the radiolabel was metabolized to volatile products in 6 months. n.s.d.[4]	System was incubated for 6 months. TEA was equally distributed between the water and the sediment. 10 to 19% of the applied radiolabel was bound to the sediment. Oxidation /Reduction potential for the sediment/water system, E_{h7} = -139 to –296 mV.	EPA RED, 1998
Laboratory Anaerobic Aquatic microcosm*	^{14}C-2-butoxyethanol (BEOH)	4.27 ppm on volume of water 11.08 ppm on weight of sediment	System : DT50 =1.4 days DT50 for 2-butoxy acetic acid DT50 = 73.3 days	n.r.[2] but in 193 days, 57.4% of the applied radio label was mineralized to $^{14}CO_2$. In 7 days, 71.8% of the applied ^{14}C-lablel was oxidized to 2-butoxyacetic acid	System was incubated for 193 days. 9.9% of the residue was bound to the sediment after 29 days. Oxidation/Reduction potential for the sediment /water system, (E_{h7}) = -200. to –296 mV. DOC was 0.3 ppm for 193 days.	EPA RED, 1998
Aqueous Field Persistence at Lake Moses	Triclopyr TEA (Garlon 3A)	0.53 gallons formulation/acre Applied July 12	n.r.[2]	The range of triclopyr concentrations was 0.02 to 0.883 ppm formulation equivalence (0.006 to 0.28 ppm a.e.). Immediately after application the concentration of –triclopyr ranged from 0.06 to 0.43 ppm formulation equivalence (0.02 to 0.14 ppm a.e.)	It is unclear if the concentration values are expressed as formulation equivalence, a.i. or a.e. applications were use to control purple loose strife at Lake Moses, Washington State.	Gardner and Grue, 1996

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT_{50})	Time to disappearance[1]	Comments	Reference
Aqueous Field Persistence at Lake Seminole, Florida	Triclopyr TEA (Garlon 3A)	1.0 ppm a.e. Applied in Winter to a 1acre plot with 1.5 meters depth (4.9 feet)	n.r.[2] Estimated DT50 = 4.5 days	Water Day 1 Surface = 0.024 ppm a.e. Middle = 0.023 ppm a.e. Bottom = 0.028 ppm a.e. Mean = 0.025 ppm a.e. Day 7 & later Mean = <0.01 ppm a.e. Sediment Day 14, 28 and 56 N.D. = <0.1 ppm a.e.	Triclopyr was applied at 1.0 ppm a.e. to control Eurasian watermilfoil but control was never higher than 50 to 60% and was considered poor. Water quality (Temperature, DOC, conductivity and pH) did not change due to treatments with triclopyr acid.	Getsinger & Westerdahl, 1984
Aqueous Field Persistence at Lake Seminole, Florida	Triclopyr TEA (Garlon 3A)	2.5 ppm a.e. Applied in Winter to a 1acre plot with 1.5 meters depth (4.9 feet)	Water n.r.[2] Estimated DT50 = 1.9 days	Water Day 1 Surface = 0.155 ppm a.e. Middle = 0.166 ppm a.e. Bottom = 0.114 ppm a.e. Mean = 0.145ppm a.e. Day 7 Surface = 0.014ppm a.e. Middle = 0.016 ppm a.e. Bottom = 0.016 ppm a.e. Mean = 0.015ppm a.e. Day 14 & later Mean <0.01 ppm a.e. Sediment Day 14, 28 and 56 n.d. = <0.1 ppm a.e.	Triclopyr was applied at 2.5 ppm a.e. to control Eurasian watermilfoil but control was never higher than 60 to 70% and was considered poor. Water quality (Temperature, DOC, conductivity and pH) did not change due to treatments with triclopyr acid.	Getsinger & Westerdahl, 1984

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT_{50})	Time to disappearance[1]	Comments	Reference
Aqueous Field Persistence at Lake Seminole Georgia*	Triclopyr TEA (Garlon 3A)	2.5 ppm Applied July 9 Applied by subsurface injection to a 10 acre segment with a depth of 1.2 meters (3.9 feet)	Water DT50 = 0.5 days	Surface Water Triclopyr concentrations Day 0, 1 & 3 2.54, 0.22 & 0.03 ppm a.e. Day 8 n.d. = <0.01 ppm a.e. TCP Concentrations Day 0 <0.05 to 0.14 ppm Day 1 <0.05 ppm Sediment 5 to 10 cm Triclopyr Concentrations Day 0 <0.1 to 0.64 ppm a.e. Day 1 <0.10 ppm a.e. TCP Concentrations Day 0 <0.025 ppm Day 1 <0.025 ppm	Treated plot was open on three sides and less than 1 Km from main channel. Extensive currents and wind generated mixing. 75% of surface area was covered with plants at time of treatment. Water quality in relationship to temperature, DOC, conductivity and pH did not vary due to the treatment with triclopyr, but it did exhibit diel patterns over the 22-days of the experiment. Water concentrations of triclopyr and TCP collected at stations 300 feet (~90 meters) outside the treated plot were similar to those found within the plot. 500 feet (~1.5 Km) downstream from treatment sit, no triclopyr or TCP was detected.	Green et al, 1989 & EPA RED, 1998 Woodburn et al, 1993

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT$_{50}$)	Time to disappearance[1]	Comments	Reference
Aqueous Field Persistence at Lake Seminole Georgia*	Triclopyr TEA (Garlon 3A)	2.5 ppm Applied July 9 by helicopter with Simplex Ball to a 10 acre segment with a depth of 1.2 meters (3.9 feet).	Surface Water DT50 = 3.3 days Bottom water 1.2 meters deep DT50 = 3.5 days Mean = 3.4 feet	Surface Water Triclopyr concentrations Day 0, 1 & 3 3.16, 1.32 & 0.28 ppm a.e. Day 21 0.03 ppm a.e. TCP Concentrations Day 0 <0.05 to 0.08 ppm Day 1 ≤0.05 ppm Bottom Water Triclopyr Day 0, 1, 3 & 42 1.35, 0.29, & <0.05 ppm a.e. TCP Day 0 & 1 <0.05 ppm Sediment Top 5 – 10 cm Triclopyr Concentrations Day 0 <0.1 to 0.21 ppm a.e. Day 1 <0.10 ppm a.e. TCP Concentrations Day 0 <0.025 ppm Day 1 <0.025 ppm	Treated plot was protected on 2 sides and was 2 to 3 Km from the main channel. Limited currents and wind generated mixing. 75% of surface area was covered with plants at time of treatment. Water quality in relationship to temperature, DOC, conductivity and pH did not vary due to the treatment with triclopyr, but it did exhibit diel patterns over the 22-days of the experiment. Water concentrations of triclopyr and TCP collected at stations 300 feet (~90 meters) outside the treated plot were similar to those foundwithin the plot. 5,000 feet (~1.5 meters) downstream from treatment sit, no triclopyr or TCP was detected.	Green et al, 1989 and EPA RED, 1998 Woodburn et al, 1993

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT_{50})	Time to disappearance[1]	Comments	Reference
Aqueous Field Persistence at Lake Minnetonka, Minnesota	Triclopyr TEA (Garlon (3A)	2.5 ppm Applied in June by subsurface injection to 16 acres with a depth of 1.98 meters (6.4 feet).	Water Triclopyr DT50 = 3.7 days TCP DT50 = 4.2 days Sediment Triclopyr DT50 = 5.0 days TCP DT50 = 11.3 days	Water Triclopyr Concentration in plot Day 1, 7 & 42 2.85, 0.44 & 0.002 ppm a.e. 100 to 800 meters of site 0.002 to 0.003 ppm a.e. at day 42 TCP Concentration in plot Day 1 & 21 0.015 & ≤0.00015 ppm 100 to 800 meters off site Day 21 & 42 0.0001 ppm a.e. TMP Concentrations in plot Day 1 & 3 0.004 ppm Sediment Triclopyr concentration Day 1, 14 & 21 0.12, 0.013 & ≤0.013 0.008 ppm at day 42 TCP Concentration Day 1-3, 14 & 21 <0.0075, 0.025 & ≤0.003 ppm	Treatment plot was Open Bay (Phelps Bay) in Lake Minnetonka. The water exchange half-life was 3.9 days hours. Water depth was 6.5 feet. At 1600 meter not more than 0.01 ppm a.e. triclopyr was detected at any time frame and <0.002 ppm a.e. triclopyr was detected on day 42. TMP is only detected through day 3 at concentrations ≤0.004. 400 meters is an adequate setback distance so that the MCLG (0.5 ppm a.e.) is not exceeded.	Getsinger et al, 2000 and Petty et al, 1998

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT$_{50}$)	Time to disappearance[1]	Comments	Reference
Aqueous Field Persistence at Lake Minnetonka, Minnesota	Triclopyr TEA (Garlon (3A)	2.5 ppm a.e. Applied in June by surface broadcast methods to 16 acres with a depth of 1.7 meters (5.5 feet).	Water Triclopyr DT50 = 4.7days TCP DT50 = 7.9 days Sediment Triclopyr DT50 = 5.8 days TCP DT50 = 10.7 days	Water Triclopyr Concentration in plot Day 1, 14 & 42 2.27, 0.295 & 0.008 ppm a.e. 100 to 1600 meters of site ≤0.006 ppm a.e. at day 42 TCP Concentration in plot Day 1 and 42 0.007 & 0.0002 ppm 100 to 400 meters Day 21 & 42 ≤0.0002 ppm a.e. TMP Concentrations in plot Day 1 & 3 0.002 and 0.004 ppm Sediment Triclopyr concentration Day 1, 14 & 42 0.19, 0.15 & <0.004 ppm a.e.	Treatment plot was an enclosed and protected Bay (Carson Bay) in Lake Minnetonka. The water exchange half-life was 6.3 days. Water depth was 5.6 feet. At 1600 meter not more than 0.01-ppm a.e. triclopyr was detected at any time frame and <0.002 ppm a.e. triclopyr was detected on day 42. TMP is only detected through day 3 at concentrations ≤0.004 ppm. 100 meter is an adequate set back distance so that the MCLG (0.5 ppm) is not exceeded	Getsinger et al, 2000 and Petty et al, 1998

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT_{50})	Time to disappearance[1]	Comments	Reference
Aqueous Field Persistence in the Pend Oreille River in a Riverine Section	Triclopyr TEA (Garlon 3A)	2.5 ppm Applied in Mid August by subsurface application techniques 6-hr. application size. 0.3 – 2.5 meters deep	Water Upper water column DT50 = 14.9 hours Lower water column DT50 = 26.4 hours Mean DT50 = 19.4 hours	Water Triclopyr in plot 1.27 ppm a.e. by day 1 <0.01 to 0.41 ppm a.e. by day 3 <0.01 ppm by day 7 300 meters down stream 0.06 ppm a.e. by day 7 675 meters down stream <0.01 to 0.47 ppm a.e. by day 1 <0.01ppm a.e. by day 7 975 meters downstream 0.02 ppm a.e. at day 0.33 <0.01 ppm at day 1	Application to control watermilfoil Proposed potable water setback distance of 400 to 800 meters is adequate	Getsinger et al, 1997
Aqueous Field Persistence in the Pend Oreille River in a Cove	Triclopyr TEA (Garlon 3A)	1.75 ppm Applied in Mid August by subsurface application techniques 4 hr. application size 0.75 to 2.8 meters deep	Water Upper water column DT50 = 47.9 hours Lower water column DT50 = 57.3 hours Mean DT50 = 52.6 hours	Water Triclopyr in plot 0.78 ppm a.e. by day 1 0.12 to 0.29 ppm a.e. by day 7 <0.01 ppm by day 14 150 meters down stream <0.01 to 0.06 ppm a.e. by day 1 0.02 ppm a.e. by day 7 395 meters down stream 0.04 ppm a.e. by day 1 <0.01ppm a.e. by day 2 975 meters downstream 0.02 ppm a.e. at day 0.33 <0.01 ppm at day 1	Application to control watermilfoil Proposed potable water setback distance of 400 to 800 meters is adequate	Getsinger et al, 1997

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT_{50})	Time to disappearance[1]	Comments	Reference
Aqueous Semi-Field Persistence in a 12 acre Bog Lake	Triclopyr BEE (Garlon 4)	0.27 lb/ acre 0.012 ppm June Application	Water DT50 = 3.8 days DT95 = 15 days Sediment DT50 greater than in water	Water Day 0 &4 2 0.012 ppm a.e. & <0.000005 ppm a.e. Sediment 100 days ~0.00012 ppm	12 Acre bog lake in Ontario at 50°North Latitude. Depth = 2.5 meters. pH = 4.5. Sandy sediment. Triclopyr adsorbs onto sediment at 100-fold lower concentrations than are in water but triclopyr does not appear to desorb from sediment.	Solomon et al, 1988
Aqueous Semi-Field Persistence in a 12 acre Bog Lake	Triclopyr BEE (Garlon 4)	2.7 lb/ acre 0.12 ppm June Application	Water DT50 = 4.3 days DT95 = 15.9 days Sediment DT50 greater than in water	Water Day 0 and 42 0.12 & <0.000005 ppm a.e. Sediment 100 days ~0.0012 ppm	12 Acre bog lake in Ontario at 50°North Latitude. Depth = 2.5 meters. pH = 4.5. Sandy sediment. Triclopyr adsorbs onto sediment at 100-fold lower concentrations than are in water but triclopyr does not appear to desorb from sediment.	Solomon et al, 1988
Aqueous Field Study at Banks Lake Washington*	Triclopyr TEA (Garlon 3A)	27 to 30 lbs a.e./acre	Water Top 1 foot DT50 = <1.0 day Bottom 3 feet DR50 = <1.0 day Mean DT50 = <1.0 day	Water TCP <0.05 ppm at surface and bottom. Sediment Triclopyr <0.1 ppm a.e. TCP = <0.05 ppm	High winds possibly accelerated triclopyr's rate of dissipation	EPA RED, 1998

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT$_{50}$)	Time to disappearance[1]	Comments	Reference
Aqueous Field Study Pond at Elk Grove CA 72 x 184 feet and 31 inches deep	Triclopyr TEA (Garlon 3A)	2.5 ppm a.e. Applied on July 26	Water Triclopyr DT50 = 6.9 days DT50 = 7.5 days TCP DT50 = 4.2 days DT50 = 4.5 days TMP DT50 = 5.3 days DT50 = 7.7 days Sediment Triclopyr DT50 = 3.4 days DT50 = 3.6 days TCP DT50 = 5.6 days DT50 = 3.8 days	Water Triclopyr 2.518 ppm a.e. at day 0.04 Day 21, 42 & 84 0.320, 0.006 & 0.001 ppm a.e. TCP 0.017 ppm at day 0.04 Day 28 and 42 0.0005 and <0.00015 ppm TMP 0.0004 at day 0.04 Day 28 and 42 0.0004 & <0.000032 ppm Sediment top 5 cm Triclopyr Day 3 0.68 ppm a.e. Day 21 & 28 0.019 & <0.003 ppm a.e. TCP Day 0.5 0.018 ppm Day 7 0.128 ppm Day 28, 42 & 84 0.008, 0.008 & <0.003 ppm TMP <0.003 ppm	12 week studies. Water quality did not change due to triclopyr treatment but seasonal changes occurred and diel changes occurred throughout the study. Sediment type was loam, clay loam and sandy clay loam.	Petty et al, 1998

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT$_{50}$)	Time to disappearance[1]	Comments	Reference
Aqueous Field Study Pond at Columbia MO 77 x 112 feet and 35 inches deep	Triclopyr TEA (Garlon 3A)	2.5 ppm a.e. Applied on June 6	Water Triclopyr DT50 = 5.9days DT50 = 6.1days TCP DT50 = 4.0days DT50 = 5.9days TMP DT50 = 4.0 days DT50 = 4.8 days Sediment Triclopyr DT50 = 2.8 days DT50 = 3.2 days TCP DT50 = 6.2 days DT50 = 7.0 days	Water Triclopyr 2.79 ppm a.e. at day 1.0 Day 21, 42 & 84 0.227, 0.007 & 0.0002 ppm a.e. TCP 0.011 ppm at day 0.04 Day 21 and 28 0.001 ppm Day 42 <0.000155 ppm TMP 0.0003 ppm at day 0.12 Day 21 and 28 0.007 & 0.0003 ppm Day 42 <0.000032 ppm Sediment top 5 cm Triclopyr Day 7 0.173 ppm a.e. Day 14 & 21 & 28 0.018 & <0.01 & <0.003 ppm a.e. TCP Day 1, 14 & 42 weeks 0.009, 0.071 & <0.003 ppm TMP <0.002 ppm	12 week studies Water quality did not change due to triclopyr treatment but seasonal changes occurred and diel changes occurred throughout the study. Sediment type was silty clay loam. Low turbidity increased light penetration, which may have resulted in more rapid dissipation due to improved photolysis.	Petty et al, 1998

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT_{50})	Time to disappearance[1]	Comments	Reference
Aqueous Field Study Pond at Lewisville TX 126 x 267 feet and 35 inches deep	Triclopyr TEA (Garlon 3A)	2.5 ppm a.e. Applied on May 31	Water Triclopyr DT50 = 6.5 days DT50 = 6.3 days TCP DT50 = 5.7 days DT50 = 10 days TMP DT50 = 6.5days DT50 = 5.7 days Sediment Triclopyr DT50 = 4.6 days DT50 = 4.6 days TCP DT50 = 13.3 DT50 = 7.0 days	Water Triclopyr 2.743 ppm a.e. at day 0.25 Day 21, 42 & 84 0.220, 0.009 & 0.0002 ppm a.e. TCP 0.020 ppm at day 1 Day 28 and 42 0.001 & <0.00015 ppm TMP 0.0004 ppm at day 0.12 Day 21, 42 and 42 0.0007, <0.00011 & <0.000032 ppm Sediment top 5 cm Triclopyr Day 1 0.264 ppm a.e. Day 21 & 42 0.018 & <0.01 & <0.003 ppm a.e. TCP Day 0.5, 7, 42 and 84 0.011, 0.159, 0.014 & <0.003 ppm TMP <0.002 ppm	12 week studies Water quality did not change due to triclopyr treatment but seasonal and diel changes occurred throughout the study. Sediment type was sandy clay loam. High turbidity decreases light penetration, which may have resulted in slower dissipation due to decreased photolysis.	Petty et al, 1998

Table 3.5
Triclopyr Persistence in Aquatic System (continued)

System	Formulation	Initial application rate	Half-life (DT$_{50}$)	Time to disappearance[1]	Comments	Reference
Aqueous Field Study in Rice field (AR) application	Triclopyr TEA (Garlon 3A)	0.375 lb a.e./acre Applied in May-June	Water 1st application DT50 = 7.6 days 2nd application DT50 = 1.8 days Soil/Sediment Top 3 inches 1st application DT50 =7.5 days 2nd application DT50 = 11.6 days	Water Day 28 at end of flood period 0.015 ppm a.e. Sediment Day 28 at end of flood period 0.026 ppm a.e.	Rice paddy applications Flooded Conditions.	EPA RED, 1998
Aqueous Field Study in Rice field (LA) application	Triclopyr TEA (Garlon 3A)	0.375 lb a.e./acre Applied in May-June	Water 1st application DT50 = 2.2 days 2nd application DT50 = 3.4days Soil/Sediment Top 3 inches 1st application DT50 = 2.9 days 2nd application DT50 = 11.7 days	Water Day 28 at end of flood period 0.006 ppm a.e Sediment Day 28 at end of flood period <0.01 ppm a.e.	Rice paddy applications. Flooded conditions	EPA RED, 1998

[1] Detection limit in is typically: water = 0.00004, 0.0001 and 0.00003 ppm for triclopyr acid, TCP and TMP, sediment = 0.003, 0.003 and 0.002 ppm for triclopyr acid, TCP and TMP

[2] n.r. = not reported

[3] system = soil and sediment residues are not distinguished in the reference

[4] n.s.d. = no significant degradation

[5] DT_{95} = time to disappearance of 95% of initial residues

[6] a.e. = acid equivalent

*= EPA guideline registration study

3.6 MICROBIAL DEGRADATION

Summary: In the field, triclopyr probably does not appreciably dissipate from the water column or sediment due to the action of aquatic microbes. Even though dissolved triclopyr acid does not readily adsorb to sediment and should be available to sediment microorganisms for degradation, the dissipation of triclopyr acid in slowly moving water appears to be primarily due to transport and dilution in the water column due to the effect of advection and dispersion. In pond waters where transport and dilution do not typically occur, other mechanisms including photolysis and microbial metabolism appear to be more important in the degradation of triclopyr, TCP and possibly TMP. However, microbial metabolism does not appear to degrade, triclopyr acid or triclopyr BEE to any great degree in laboratory aerobic and anaerobic aquatic microcosms (EPA, RED, 1998). For example, triclopyr acid and triclopyr BEE degrade in aerobic and anaerobic aquatic microcosms with extrapolated half-lives of 142 and 1,300 days, respectively.

The TEA moiety dissociated from triclopyr TEA and the BEOH moiety hydrolyzed from triclopyr BEE appear to be rapidly metabolized under aerobic conditions. For example, the DT95 for TEA is 18 days and 60% of the applied ^{14}*C-TEA label is degraded to* $^{14}CO_2$ *in 18 days. Also, under aerobic conditions, the half-life of BEOH is 0.6 to 3.4 days and the half-life of its metabolic intermediate 2-butoxyacetic acid is only 1 day; after 10 days, ~70% of the applied* ^{14}*C-BEOH has been metabolized to* $^{14}CO_2$*.*

Under anaerobic aquatic conditions, TEA and BEOH degrade much more slowly. TEA degrades to unspecified degradates under anaerobic aquatic conditions with an extrapolated half-life of 2 years. While BEOH degrades to 2-butoxyacetic acid under anaerobic conditions with a half-life of 1.4 days, the DT50 for 2-butoxyacetic acid is 73.3 days. It takes approximately 193 days for ~57% of the applied BEOH to be mineralized to carbon dioxide.

It seems likely that triclopyr is also degraded on soils by microbes. When applied at 1 ppm to silty clay loam or silt loam soils microcosm, triclopyr is degraded to 3,5,6-trichloro-2-pyridinol (TCP) and 3,5,6-trichloro-2-methoxypyridine (EPA RED, 1998). The half-life for degradation of triclopyr on the named soil types is 8 to18 days, respectively. The metabolites do not appear to be persistent and were not seen after 30 days of incubation. The ultimate degradate is carbon dioxide with 70% to 80% of the applied radioactivity being tranformed to $^{14}CO_2$ *in 300 days.*

From the field studies discussed above, it is apparent that microbes and possibly photolysis may degrade triclopyr and its main metabolite (TCP) as well. This may be particularly important on terrestrial soils. However, in water triclopyr and its metabolites may not be degraded effectively by sunlight at depths of greater than 15 cm and although degradation due to microbial metabolisms cannot be ruled out, dissipation due to transport and dilution in water seems to be the more likely dissipation scenario particularly in slow moving aquatic systems [lakes and rivers (Green et al, 1989; Petty et al, 1998; Getsinger et al, 2000 and Getsinger et al, 1997)] where advection and dispersion due to water flow occurs. Microbial action is probably more important and may be the dominant mechanism in ponds where little inflow or outflow of water occurs. However, this is only conjecture and has yet to receive vigorous scientific investigation (Petty et al, 1998).

Racke et al (1988) has noted that TCP is degraded on several (four) Midwestern corn soils. The half-lives of ^{14}*C-TCP on these soils ranges from 8 to 12 days and the main metabolite appears to be* $^{14}CO_2$ *which is seen at levels of 62% to 80% of the applied radiation within 14 days of application. Another 6 Midwestern corn soils do not appear to rapidly degrade TCP. These soils have half-lives that are considerably longer than 14 days and only produce ~5% to 20%* $^{14}CO_2$ *from* ^{14}*C-TCP after 14 days of incubation. While these microbes appear to rapidly degrade TCP when it is at concentrations of 5.0 ppm, concentrations as low as 50 ppm TCP greatly reduce the rate at which TCP is degraded. Although this breakdown of* ^{14}*C-TCP to* $^{14}CO_2$ *is likely to be due to microbes that can use TCP as a sole carbon-energy source, Racke et al (1988) was unable to detect these microbes.*

Feng et al(1997) found that a Pseudomonas *species related to* Pseudomonas corrugata and Pseudomonas marginalis *were able to degrade* ^{14}*C-TCP and most photolysis products of* ^{14}*C-TCP could be degraded to carbon dioxide (Feng et al, 1998). After TCP is formed, it can be further metabolized by microbes, eventually forming carbon dioxide as an end product or forming 2-hydroxypyridine through a photolytic reductive dechlorination and then undergoing ring cleavage to form 4-oxo-4-(amino)-2-buten-1-aldehyde. This product can be transformed by further photolysis or metabolism by* Pseudomonas *sp. to carbon dioxide, water and ammonium ion. Alternatively, chlorine can be retained in the ring to form various dichlorodihdroxypyridines, which then form various chlorinated 4-carbon straight chain alkenes with a triple bonded nitrogen. All of these photoproducts can be degraded to carbon dioxide* by Pseudomonas *sp. except for the dichlorodihydroxypyridines.*

It seems likely that several species known to degrade the related herbicide (2,4-D) may also be capable of degrading triclopyr to non-toxic metabolites. These species include Acaligenes eutrophus, Arthrobacter *sp.,* Bordetella *sp.,* Flavobacterium *sp.,* Pseudomonas *sp.* and Xanthobacter *sp. (Section 3 of 2,4-D SEIS).*

The above discussion would tend to indicate that species of microbes not capable of utilizing triclopyr as a sole carbon-energy source are also important in metabolizing triclopyr and TCP in soil and water. A variety of microorganisms may be needed to achieve complete degradation of triclopyr and its metabolite TCP combined with photolytic and other non-biotic degradation mechanisms. This consortium of bacteria could be important not only in degrading triclopyr and TCP in natural soil and water/sediment environments, but also in degrading triclopyr and it metabolites in water treatment and sewage processing plants (Feng et al, 1998)

Some microflora can probably utilize triclopyr as their sole carbon-energy source, and others can metabolize triclopyr, but it is not clear if they can utilize it as their sole carbon-energy source. There have been no specific microbes identified as capable of degrading triclopyr. However, a *Pseudomonas* species has been noted to degrade TCP and its photoproducts to carbon dioxide, water and ammonium ion (Feng et al, 1997 and Feng et al, 1998). This species of bacteria appears capable of utilizing TCP as a sole carbon-energy source.

Several species of microbes that are known to degrade the related herbicide (2,4-D) may also be able to degrade triclopyr to non-toxic metabolites. These species include *Acaligenes eutrophus, Arthrobacter* sp., *Bordetella* sp., *Flavobacterium* sp., *Pseudomonas* sp. and *Xanthobacter* sp. (Section 3 of 2,4-D SEIS). However, none of these species may be capable of utilizing triclopyr as a sole carbon-energy source (Section 3 of 2,4-D SEIS).

However, since no individual species of microbes has been noted to utilize triclopyr as sole carbon-energy source, a number of microorganisms could be important, not only in degrading triclopyr and its subsequent degradates in natural soil and water/sediment environments, but also in degrading triclopyr and its metabolites in water treatment and sewage processing plants (Feng et al, 1998).

The only studies that indicate that microbes may be involved with the degradation of triclopyr acid and triclopyr BEE in water/sediment ecosystems are laboratory aerobic soil, aerobic aquatic and anaerobic aquatic studies. Triclopyr acid is formed from the dissociation of triclopyr TEA and hydrolysis of triclopyr BEE.

After dissociation or hydrolysis, triclopyr acid is slowly degraded under aerobic aquatic conditions. The estimated half-life for the degradation of triclopyr under aerobic conditions is 142 days. At the end of 30 days, only 5% of the applied ^{14}C-label is converted to TCP. Under anaerobic aquatic conditions , triclopyr acid hydrolyzed from triclopyr BEE is slowly metabolized with a half-life of 1,300 days. Only 25% of this applied ^{14}C-label is converted to TCP in 365 days. TCP is generally assumed to be a microbial degradate of triclopyr (EPA RED, 1998). Since the main metabolite in field studies is also TCP, microbial degradation of triclopyr is assumed to be important in the field. Another metabolite, TMP may also be formed from the microbial degradation of TCP but it is not clear if TMP is produced by further degradation of TCP or by some other mechanism directly from triclopyr acid (Green et al, 1989; Petty et al, 1998 and Getsinger et al, 2000).

The dissociation of triclopyr TEA produces TEA and the hydrolysis of triclopyr BEE produces BEOH. The TEA and BEOH moieties are also degraded rapidly in aerobic water/sediment systems. Under aerobic aquatic condition, TEA is probably degraded by microbes to carbon dioxide with more than 60% of the applied ^{14}C-TEA label mineralized to $^{14}CO_2$ in 18 days. The DT95 for the degradation of TEA is 18 days and there is a lag period of 14 days when very little degradation occurs (<2% mineralization to $^{14}CO_2$). This lag phase indicates that microbial degradation is a likely mechanism for the degradation of ^{14}C-TEA to $^{14}CO_2$. Under aerobic conditions the formation of the BEOH hydrolysis product is also rapid. The half-life for the conversion of BEOH to the metabolic intermediate (2-butoxyacetic acid) ranges from 0.6 to 3.4 days and the half-life for the degradation of 2-butoxy acetic acid is approximately 1 day. Approximately 70% of the applied 14C-BEOH label will be mineralized to $^{14}CO_2$ in less than 10 days in an aerobic aquatic microcosm (EPA RED, 1998)

Both the TEA dissociation product and the BEOH hydrolysis product are much more persistent under anaerobic than aerobic aquatic conditions. ^{14}C-TEA has an extrapolated half-life of 2 years under anaerobic aquatic conditions and no significant degredation of ^{14}C-TEA to $^{14}CO_2$ was seen during the first 6 months of incubation. ^{14}C-BEOH is also degraded more slowly under anaerobic aquatic condition. BEOH is transformed to 2-butoxyacetic acid with a half-lie of only 1.4-days but the half-life of this metabolic intermediate is approximately 73 days. The ultimate product was $^{14}CO_2$, which was 57.4% of the applied ^{14}C-BEOH at the end of the study (193 days after treatment).

Unidentified bound residues, usually less than 10% of the applied label, may be natural products of microbial metabolism which have been incorporated into the sediment. Such natural products may include humic and fulvic acids which are the end products in the metabolism of many pesticides.

Microbial action in soil may also degrade triclopyr. Triclopyr acid applied at 1ppm a.e. on soil has a half-life of 8 to 18 days of silty clay loam and silt loam soils, respectively. The main metabolites include TCP and TMP at maximum concentrations of 26% and 8%, respectively. These soil metabolites do not appear to be persistent and were not seen after <30 days of incubation. After 30 days of incubation, 70% to 80% of the applied $^{14}CO_2$-triclopry acid was mineralized to $^{14}CO_2$.

The main metabolite generated from the probable action of soil bacteria is TCP. This metabolite has been noted in laboratory experiments to degrade on a number of Midwestern corn soils (four with a half-life of 8 to 12 days. Bacteria are assumed to use this metabolite as a sole carbon-energy source since 62% to 80% of the applied ^{14}C-label was converted to $^{14}CO_2$ in only 14 days. Other Midwestern corn soils (6) did not appear as effective in degrading TCP to carbon dioxide. These less metabolically active soils degraded ^{14}C-TCP with a half-life of >14 days and only produced 5% to 20% carbon dioxide from ^{14}C-TCP after 14 days of incubation. Although attempts were made to detect bacteria that were capable of degrading TCP and using it as a sole carbon-energy source, these experiments were not successful. TCP appears to have a low level of antibacterial activity. Five ppm of 14C-TCP in the soil was degraded to $^{14}CO_2$ in 14 days at levels of 62% to 80% of the applied radiation. However, 50 ppm TCP appeared to be somewhat toxic to these bacteria with only 4% of the applied ^{14}C-TCP mineralized to $^{14}CO_2$. At even higher concentrations (100 ppm TCP), almost complete inhibition of pesticide (isofenphos and carbofuran) metabolism was seen in the resident microbial population (Racke et al, 1988).

Since these studies were conducted in the dark, the formation of carbon dioxide from triclopyr acid, TEA TCP or BEOH indicates that microbes are probably involved with the degradation of these materials in the laboratory. Since TCP and TMP are also seen in both terrestrial and aquatic field dissipation studies, it is likely that microbes are involved with these degradations. However, it is not clear to what degree microbial degradation is involved with the degradation of triclopyr acid to TCP and TMP in aquatic field situations since mass balance studies are not practical in most field situations. Also, in situations where even a slow water flow occurs, dissipation of triclopyr and its metabolites from both the water column and the sediment may have more to do with the advection and dispersion caused by this flow than by the effects of microbial metabolism (Petty et al, 1998 and Getsinger et al, 1997). In ponds, microbial degradation and photolysis may play a more important role since triclopyr and its metabolites largely dissipate from the water column of these ponds in less than 42 days even when the inflow and outflow of water from the treated ponds is limited.

3.7 MOBILITY

<u>Summary</u>*: The data reviewed dealt with both adsorption and desorption triclopyr acid, triclopyr TEA, triclopyr BEE and the microbial metabolite TCP (3,5,6-trichloro-2-pyridinol). The triethylamine (TEA) moiety and the 2-butoxyethanol (BEOH) moiety, were not tested for mobility because of their rapid dissipation on aerobic soils and sediments (EPA, RED 1998). A few adsorption/desorption studies have been produced*

to support the registration of triclopyr products and some studies are also available from the open literature. In most soils, adsorption is very low. Soil/water partition coefficients have been observed to vary from 0.01 L/Kg for a Hammond surface soil with an organic carbon content of 3.4% to 1.32 L/Kg for a sandy clay loam containing an organic carbon content of 2.4% (Obenshain et al, 1997 in Abdelgehani, 1995, Reeves, 1995). The highest adsorption was on a forest organic peaty soil containing 40% organic carbon; the Kd_{ads} *for this soil had e a mean value of ~16 L/Kg (Jotcham et al, 1989).*

The Kd_{ads} *values were similar in tests of triclopyr acid and triclopyr BEE. The observed* Kd_{ads} *values for triclopyr TEA and triclopyr acid were an order of magnitude lower than the observed* Kd_{ads} *values for triclopyr BEE. However, this may have been an artifact of experimental design and it is not clear whether triclopyr acid or triclopyr TEA was tested in some cases. The observed Freundlich* K_{ads} *values and the Freudlich* K_{des} *values are not significantly different from the previously described* Kd_{ads} *values for triclopyr products. However, the* Kd_{des} *values for soils aged for 15 to 30 days are typically 2- to 3-fold higher (Freundlich* $K_{des} = 0.87$ *to 5.3 L/Kg) than the Freundlich* K_{des} *values observed on un-aged soil (Freundlich* $K_{des} = 0.34$ *to 1.4 L/Kg). This indicates that triclopyr products have less tendency to desorb and leach after they have aged on soil for 15 to 30 days (Woodburn et al, 1988). Generally, if the soil/water distribution coefficient is greater than 5 a pesticide is considered to be immobile. Triclopyr is known to adsorb poorly to all soil types except forest peaty soil. Therefore, under typical use conditions, triclopyr products and their TCP metabolite will be mobile after adsorption to sediment or soil surfaces. Leaching of triclopyr is likely to be high because of the weak adsorptive capacity of these soils and sediments. The pH appears to have a strong impact on the adsorption of triclopyr to soils obtained from Arkansas rice growing regions, In both natural soils and those that had their pH altered, triclopyr acid has sorbed more strongly to soils with low pH (pH ~5.0) than soils with high pH (pH ~7). However, in both high and low pH situations the observed* Kd_{ads} *or Freundlich* K_{ads} *values remain low (K values at pH 5 = 0.51 to 1.73 L/Kg; K values at pH 7 = 0.08 to 0.76 L/Kg). Therefore, the mobility of triclopyr products will be high and the leaching potential great at all environmentally relevant pH (Johnson et al, 1995).*

Organic matter and CEC both appear to increase the amount of adsorption of triclopyr products. However, soil parameters interact, making it difficult to pinpoint a single cause for high or low sorption in most studies. Nevertheless, it is likely that Triclopyr will bind moderately to sediments with high cation exchange capacity or high organic carbon content. Both soils with large amounts of clay and soils with a high organic carbon content usually have high CEC values as well. If organic carbon content is the primary factor influencing adsorption of triclopyr, it should adsorb more readily at low pH; due to more triclopyr being in the non-ionized form. Work with soils at both high and low pH indicates that organic matter is probably the main factor influencing sorption of triclopyr (Johnson et al, 1995). However, extensive adsorption of triclopyr to soil or sediment only occurs on those soils with very high levels of organic carbon. Many lake bottoms have fluffy, light (flocculent) sediments and considerable amounts of suspended sediments rather than a solid surface. The much larger amount of particle surface in these flocculent sediments greatly increases the likelihood of that triclopyr or other aquatic herbicides will adsorb compared with firm-surfaced sediment, provided that these flocculent and suspended sediments have high organic carbon content. Field studies do not indicate that turbidity greatly impacts the amount of triclopyr removed from the water column.

Mobility of triclopyr within the water column may also be affected by the sorption of triclopyr to aquatic macrophytes. It has been estimated that target plants like Myriophyllum spicatum *can concentrate triclopyr in tissues at levels 10-fold-higher than seen in the water column. However, non-target plants like* Potamogeton zosteriformis *do not concentrate triclopyr against the water gradient (Getsinger et al, 2000). It seems unlikely that these plants (after dying) would re-release enough triclopyr to adversely impact plants or other aquatic species. Although no work has been done on the metabolism of triclopyr in aquatic plants, it has been observed on terrestrial grasses and rice commodities that triclopyr is not metabolized; only triclopyr is seen as a terminal residue on grass and rice commodities and no significant levels of the metabolites TCP or TMP have been detected (EPA RED, 1998).*

Overall evidence indicates that at typical environmental concentrations, triclopyr and its TCP metabolite bind weakly and reversibly to most soils and sediments. Since both triclopyr and TCP appear to be persistent in the water column and are considered to be mobile, the EPA believes that these chemicals have potential to leach into the ground water (EPA RED, 1998). Further evidence of potential leaching has been provided by soil column studies which indicate that 1 inch of "rain" added every other day to the column will cause 100% of triclopyr BEE and 65% of triclopyr acid to leach through a 16 inch column of sand in 30 and 54 days, respectively (Lee et al, 1986). Reeves (1995) found similar results with 12 inch sand, loamy sand or sandy loam columns after 8 inches of "rain" was applied over a 2-day period; these soils contained only low levels of organic carbon (1.1 to 2.7%), so leaching was not unexpected. However, Lee et al (1986) found that triclopyr acid and triclopyr BEE did not leach as readily in forest soils containing 34% organic; 59% to 60% of the applied radioactivity remained in the columns with most of this (81% to 88% of the recovered radiation) being transformed to TCP. It is not clear if the remainder of the radiation leached out of the column or was mineralized to $^{14}CO_2$.

Aging of triclopyr BEE on 12 inch sand columns causes less of the applied triclopyr to leach from the soil column. Thirty-six percent, 23% and 15% of the applied radiation leached from these columns in 31, 90 and 124 days, respectively. Almost all leached radioactivity in columns aged for 31 days was recovered as triclopyr acid. However, only half of the leached radiation was recovered as triclopyr after 90 or 124 days of aging. Only small amounts of the leached radiation (3% to 6% of the applied) was recovered as TCP (Reeves et al, 1995).

There are also experiments that indicate that triclopyr BEE does not generally leach in soils typically found in the field. Application of 1.8 lbs a.e./acre was applied to lysimeters that were 3 - 4 feet deep and contained sandy soil sown with rough grass. One percent of the applied radiation was found in the leachate after 2 years. Only very small amounts of triclopyr acid (0.00007 ppm a.e.) and TCP (0.00007 ppm) were found in the leachate waters. The amount and intensity of rainfalls were not specified.

In field studies at Northern Ontario forestry sites, triclopyr was applied at rates of 2.5 to 3.6 lbs/acre to a sandy soil containing up to 34% organic matter (19% organic carbon) and at rates of 2.2 to 2.8 lbs/acre to a clay soil containing up to 74% organic matter (43% organic carbon). Up to 60 days after application, 97% of the triclopyr was recovered in the top 6 inches of soil where 7 to 10 inches of rain had fallen. There was no evidence for lateral mass movement of triclopyr down slope in the soil; triclopyr concentrations in soil from 1 to 2 meters off-site were not seen at levels higher than the *limit of detection (<0.00054 ppm a.e.). Very little triclopyr was found in the water (0.00001 to 0.00096 ppm a.e.) of artificial drainage ditches located 12 to 13 meters down slope from the edge of the treatment site (Stephenson et al, 1990).*

Although the mobility and persistence of triclopyr and TCP triggers ground water concerns, the limited amount of monitoring indicates that only 5 detections were reported from 379 wells located in 2 states. The levels of triclopyr found in these wells was far less than the MCLG of 0.5 ppm a.e. Triclopyr acid was never found in these wells at concentrations higher than 0.000006 to 0.00058 ppm a.e. (Hoheisel et al, 1992 in EPA, RED, 1998). In various places throughout the state of Washington, the ground water was monitored for the presence of triclopyr. No triclopyr was detected at the any of the tested sites during the 1988 to 1995 time period. The related herbicide (picloram) has been detected at 2 of the 243 sites tested at a maximum concentration of 0.00007 ppm and picloram has a MCLG (0.5 ppm) that is the same as that for triclopyr (Larson, 1996).

Triclopyr was detected in the surface water of some small streams in the Puget Sound region during the 1987 to 1995 time frame. Thirteen sites spread throughout the Puget Sound region were monitored. Concentrations of triclopyr ranged from ~0.000006 to ~0.001 ppm and this is much below the levels that that are likely to affect aquatic life (USGS, 1997 and USGS, 1999).

When a triclopyr is applied to soil, there is significant potential for the chemical to be carried downward with water movement from rain and irrigation. Pesticides exhibit a wide range of leaching potential, from those that adsorb strongly to soil particles and are not released before they break down, to those that do not adsorb significantly (or adsorb, then desorb) and will travel considerable distances down through the soil, sometimes as far as the ground water table. The sorption of various chemicals to soil is affected in a number of ways by soil parameters such as organic matter, clay content and type, and pH. Triclopyr and its major metabolite (TCP) are known to be mobile based on their typical soil/water adsorption coefficients (Kd or Freundlich K). On un-aged soils, the Kd is typically less than 2.0 L/Kg (Table 3.2.5). Furthermore, triclopyr and its TCP metabolite have leached through 12 inch soil columns containing soils with low organic carbon content (1.1% to 2.7%) after only 8 inches of “rainfall”; ~60% to ~90% of the applied triclopyr BEE was detected in the leachate primarily as triclopyr acid (Reeves, 1995).

In lysimeter and field studies designed to mimic real life situations, triclopyr and TCP were not found to leach through a 3.4 foot deep sandy soil column sown with rough grass prior to an application of 1.8 lbs a.e./acre triclopyr BEE (Reeves, 1995). Only 1% of the applied label was found to leach out of the lysimeter during the course of the 2-year study. Concentrations of triclopyr and TCP were not higher than 0.00007 ppm for each analyte. Approximately 85% of the applied radiation was found in the top 12 inches of the soil in the lysimeter study; the majority of this was irreversibly bound, indicating a strong adsorption of any remaining residues found in the soil. This is confirmed by Freundlich K_{des} values that are typically 2- to 3-fold higher (0.58 to 4.53 L/Kg) after aging for 15 to 30 days when compared to Freundlich K_{des} values measured immediately after application (0.34 to 1.17 L/Kg). Also confirming this observation is that leaching decreases progressively, after 8 inches of “rain”, through a 12 inch soil column as the laboratory applied radioactivity is aged from 31days (36% leached) to 90 days (23% leached) and 124 days (7% leached) (Reeves, 1995).

In field studies conducted at forestry sites in Northern Ontario, triclopyr BEE at ~2 to ~ 4 lbs/acre was applied to high organic matter sand (~33% = 19% organic carbon) and high organic matter clay soils (74% = 43% organic carbon). After 60 days with a total rainfall of 10 and 7 inches, respectively, 97% of the triclopyr was recovered within the top 6 inches of a soil core. More than 90% of the triclopyr acid was recovered from the upper organic layer of these forest soils. No off-site lateral mass movement of triclopyr was seen in soils located 1 to 2 meters from the edge of the application site. The concentrations of triclopyr in these off-site soils was less than the limit of detection (<0.00054 ppm a.e.) In artificial drainage ditches located 12 to 13 meters down slope from the edge of the treatment site, only 0.00001 to 0.00096 ppm a.e. triclopyr was found in the drainage water. This represents typical effects that would be seen in typical forest contours with slopes of 7° to 8° (Stephenson et al, 1990).

Controlled laboratory "batch equilibrium" studies are designed to measure the adsorptive properties of pesticides to 4 representative soils (EPA RED, 1995). There are currently no comparable test guidelines specifically for sediment and no true sediments appear to have been tested with triclopyr acid, triclopyr TEA, triclopyr BEE or the TCP metabolite for sorptive capacity. The results for these tests on a number of soils are presented in Table 3.7. Both adsorption (K_{ads}) and desorption coefficients (K_{des}) have been reported. The amount of adsorption that occurs with all of the triclopyr products and TCP is minimal (Kd_{ads} and Freundlich K_{ads}) under most situations. The adsorption coefficient value for triclopyr typically varies from 0.01to 1.32 L/Kg on soils with low organic carbon content (0.41 to 3.4%). High adsorption coefficients (15 L/Kg) were only seen in high organic carbon content peaty soils (40.3%). Desorption coefficients (Kd_{des} and Freundlich K_{des}) were also low for triclopyr acid when the soils were not aged after application. Under non-aged conditions, the Freundlich K_{des} ranged from 0.34 to 1.4 L/Kg. However, after aging for 15 to 30 days, these desorption coefficients increased to values of 0.87 to 5.3 L/Kg. This partially explains why column leaching, lysimeter and field data show less leaching of triclopyr than is expected from the physical properties of the herbicide alone. However, the metabolite TCP does not appear to sorb well under non-aged or aged conditions. For example, the Freundlich K_{ads} of TCP ranges from 0.53 to 1.95 L/Kg and the Freundlich K_{des} ranges from 0.18 to 0.58 L/Kg after 30 days of aging. The soil partition coefficients (Kd_{ads} and Kd_{des}) are measures of the potential for adsorption to and desorption from soil, and are calculated as the chemical concentration in soil divided by the concentration in water at equilibrium in a soil/water system. The Freundlich K_{ads} and Freundlich K_{des} are another way of calculating leaching potentials, but use the results of a series of tests with different starting concentrations. The parameters are particular to the specific soil being tested. To calculate Kd_{ads} and Freundlich K_{ads}, biologically active soil plus water containing radio-labeled chemical are put in a sealed vial and shaken slowly for several hours until an adsorption equilibrium is reached (no more chemical can be adsorbed by the soil). The amount of chemical in the water and soil is determined by measuring the radioactivity in each. If Kd_{des} and Freundlich K_{des} values are determined, the water is then removed, replaced with fresh water, and the vial shaken again to allow the chemical to desorb from the soil back into the water. From measurements then taken, the Kd_{des} is calculated in the same manner as Kd_{ads}.

Although there is some disagreement as to exact classification values, generally Kd_{ads} and Freundlich K_{ads} values greater than 5 are characteristic of compounds that are considered to be not appreciably mobile. Values from about 1 to 5 indicate a potential for greater mobility, while values less than 1.0 denote considerable mobility potential. In a similar manner, high Kd_{des} and Freundlich K_{des} values or a low percentage of desorbed pesticide indicate that an adsorbed compound will remain bound to soil and resist being carried downward.

Kd and Freundlich K values are composite values measuring adsorption caused by any of several soil characteristics such as clays, aluminum content, cation exchange capacity (CEC), and organic carbon. Koc values represent an attempt to separate out the role of organic carbon in soil adsorption from the other factors. Because organic carbon plays a significant role in the soil adsorption of many pesticides (Leng et al, 1995), Koc values are often used to predict pesticide mobility. But since Koc depends on two variables (Kd and carbon content), it must be used with caution. In the case of triclopyr, the adsorption correlates well with organic matter content work done at some laboratories (Jotcham et al, 1989; Reeves, 1995 and Johnson, 1995) but not others (Woodburn et al, 1988). However, in all cases where the organic carbon content was less than 4%, triclopyr adsorption was low (Kd or Freundlich K_{ads} ≤1.32 L/Kg); in these cases triclopyr would be considered mobile with a high potential to leach into the groundwater. However, on forest soils with organic carbon content of ~41%, triclopyr adsorption was seen to be high (Kd or Freundlich K_{ads} =15.5); in this case triclopyr would be considered to be immobile with very low potential to leach into the ground water.

Koc values are calculated by dividing Kd and Freundlich K values by the decimal percent of organic carbon in a soil [e.g. for a peat soil (Jotcham, 1989), Koc_{ads} is calculated as 15.5/0.403 = 38.5 L/Kg. Koc values may give an idea of the importance of organic carbon in a soil or sediment in adsorbing a chemical. Koc values always are numerically higher than Kd or Freundlich K values. A higher value indicates organic carbon is more influential in trapping a pesticide. For instance, in Table 3.7 a number of authors give Koc values for triclopyr that range from 1.05 L/Kg to 780 (Obenshain et al, 1997 in Abdelgehani, 1995; Woodburn et al, 1988, Wauchope et al, 1992, and Ritter and Peacock, 2000). The lower values are probably not very accurate since the amount of triclopyr adsorbed to the soil is negligible (Abdelgehani, 1995 in Obenshain et al, 1997). Rapid conversion of triclopyr TEA and triclopyr BEE to triclopyr acid, causes the K_{oc} values to be similar for all products providing the only soil variable is soil organic carbon content. The Koc value varies by over 3 orders of magnitude indicating that organic carbon content is not the main factor that governs triclopyr adsorption. It has been reported by Wauchope et al (1992) that the Koc for triclopyr TEA can only be estimated at 20 L/Kg because an unusually wide range of values has been reported in the literature. Wauchope et al (1992) reported the Koc value for triclopyr BEE (which is rapidly converted to triclopyr acid) to be 780 L/Kg; but Reeves (1995) found that typical Koc values for triclopyr BEE are ~50 L/Kg. It is clear from this data that triclopyr is likely to be mobile. This high mobility may lead to extensive leaching but because it is not bound tightly to soil triclopyr should be readily available to microbes to degrade and use as a sole carbon-energy source (EPA RED, 1998 and Feng et al, 1998 and Feng et al, 1997).

Although leaching potential is indicated by the data presented in the previous paragraph, triclopyr has not leached extensively in field studies. The lack of leaching potential is surprising since triclopyr is an organic acid that should be susceptible to leaching (Branham et al, 1994). Lack of leaching potential has been shown on high organic matter (>34 to 74%) forest soils (Stephenson et al 1990), lysimeter studies (Reeves, 1995) and field soil dissipation studies where triclopyr and TCP have been observed in soil and leaf litter as deep as 90 cm (35 inches). TMP was also observed in field dissipation and forestry studies but was not observed in soil or leaf litter below 30 cm (12 inches). This should not present a ground water issue except where the water table is extremely shallow (EPA, RED, 1998). Triclopyr was not detected on agricultural soil in North Carolina or California below 45 cm (18 inches) and 15 cm (6 inches) inches, respectively, while TCP and TMP were not detected below 30 cm (12 inches) and 15 cm (6 inches), respectively.

All of the "K" parameters discussed above are specific to a particular soil or sediment, and to the initial concentration of a chemical applied to the soil or to a sediment/water system. A Freundlich K for a particular soil is a single value calculated using the adsorption or desorption results from all of the initial concentrations used in an experiment, but a Kd is calculated from the result of each initial concentration separately. Unless specified otherwise, Kd and Freundlich K parameters reported in published literature are for adsorption; measurement of desorption values is rare. Where K values are given without the soil type and chemical concentration being specified, care should be exercised in using those values for evaluation of leaching potential.

3.7.1 Soil and Sediment

The adsorption constants (Kd and Freundlich K) located during this review deal only with soils. Sediments were not tested for adsorption constants. However, rice paddy soils were tested (Johnson et al, 1995). Soil mobility data are directly relevant to the expected behavior of triclopyr over-sprayed on shoreline vegetation and to some extent indicates what may happen if a lake level drops, exposing shoreline sediment to drying, soon after treatment. Soil data can also be reasonably extrapolated to predict to some extent the adsorption of triclopyr on pond and lake sediments. Sediment will usually have a higher organic matter content than soils. However, soil tests of higher organic content soils could be used as a guide to anticipate the potential for triclopyr adsorption to some sediments. Unfortunately, the percent organic matter and CEC are often not indicated in studies where soil/water adsorption coefficients were calculated.

The EPA RED (1995) discusses mobility studies that were conducted according to EPA laboratory guidelines to determine the adsorption constants in 4 representative soils. Each of the 4 soils was mixed with water to form a slurry, then ^{14}C-triclopyr acid was added to make several unspecified initial concentrations. After agitation for period of time long enough to obtain equilibrium, Freundlich K values were calculated for each set of concentrations for a given soil (Table 3.7).

In all of the soils with organic carbon levels less than 4%, the K_{ads} values were very low (0.012 to 1.32) indicating that triclopyr was weakly adsorbed to the soils and would be readily desorbed back into solution. Triclopyr sorption appears to be loosely correlated with organic carbon levels in the soils and other factors (particularly pH) appear to have a strong influence on the adsorption of triclopyr. At pH 7, triclopyr adsorbs only slightly (Kd_{ads} = 0.08 to 0.23 L/Kg) but at pH 5 triclopyr still adsorbs only slightly but at higher levels (Kd_{ads}= 0.51to 0.59 L/Kg). This can be explained by noting that at pH 7 more of the triclopyr is in a free acid or conjugate base form, while at pH 5 more of the triclopyr is in the acid form. However, since the pKa of triclopyr is 2.68, more than 50% of the triclopyr will exist as the free acid of conjugate base at a pH higher than 2.68. At a pH of ~2.0, it would be expected that almost all of the triclopyr would be in the acid form and that the Kd_{ads} values would reach a maximum that may be predicted by the Huffaker equation (Johnson et al, 1995). Desorption of triclopyr is generally very high on un-aged soils (Freundlich K_{des} = 0.34 to 1.17 L/Kg) but aging of triclopyr on soil decreases the amount of desorption that is likely to occur (Freundlich Kd_{des} = 0.87 to 5.3 L/Kg after 15 days aging to 0.95 to 4.53 L/K after 30 days aging). This indicates that when triclopyr is aged on soil for 15 to 30 days, the likelihood of leaching may decrease significantly on some soils (Woodburn et al, 1988). This lack of leaching of aged residues has been demonstrated in the field on lysimeters, forest soils and agricultural soils (Reeves, 1995; Stephenson et al, 1990 and EPA RED, 1998).

The triclopyr metabolite TCP, adsorbs only slightly (Kd_{ads} = 0.53 to 1.95) (EPA, RED, 1998) and desorbs readily (Freundlich K_{des} = 0.18 to 0.58) (Woodburn et al, 1988) after 30 days of aging . Such low desorption coefficients would indicate that TCP should readily leach. However, like triclopyr, TCP does not readily leach; as described above, the metabolites TCP and TMP do not readily leach and are not seen in forestry and agricultural soils below 30 cm (12 inches) (EPA RED, 1998).

Ritter and Peacock (2000) have reported that typical soil Koc values range around 53 L/Kg, which would yield soil Kd values from 0.5 to 2.0 L/Kg on soils containing 1.0% to 4% organic carbon. It is not clear what soil properties other than organic matter and pH may influence adsorption and desorption of triclopyr and TCP (Johnson et al, 1995). Other soil properties, such as clay mineral content, silt content, sand content or cation exchange capacity (CEC) do not appear to substantially impact the adsorption of triclopyr.

Another method of determining if a herbicide is adsorbed and not easily leached is applying the pesticide to the top of a soil column packed with environmentally relevant soils. When soil columns are packed with sand and the treatment rate is 5.0 lbs/acre, a rainfall of 1inch every other day will leach 100% of the applied ^{14}C-triclopyr BEE through a 29 inch soil column in 30 days. The same treatment and environmental parameters will leach 65% of the ^{14}C-triclopyr acid through a 29 inch soil column in 54 days with 9.75% of the applied triclopyr acid retained in the column and 25% unaccounted for (possibly volatile like CO_2). Lee et al (1986) found that similar experiments with soils containing 34% organic matter did not leach triclopyr and that almost all of the triclopyr BEE or triclopyr acid had been metabolized to TCP (~80% to 90% of the recovered radiation) with the remainder of the recovered radiation recovered as TMP (6% to 15%) and triclopyr acid (4% to 5%). Leachate data was not documented, but presumably, no radioactive material was leached from these columns with ~60% to 65% of the applied radiation being found in the top 4 inches of the column. However, in soils not containing siginificant amounts of organic carbon (1.1% to 2.7%), 57% to 87% of the applied radioactivity was leached through 12 inch soil columns after the application of 8 inches of “rainwater” (Reeves, 1995).

The decreased mobility of triclopyr acid, due to the effects of aging, was confirmed by treatment of 12 inch columns containing no significant organic carbon and aging these residues for 31, 90 and 124 days. The total leachate seen in these columns was 36%, 23% and 15%, respectively. The majority of the leached applied radiation was triclopyr acid (30%, 10% and 7%, respectively) with the remainder being TCP and an unknown metabolite (Reeves et al, 1995). With increasing aging time, more of the ^{14}C-labeled residues remained in the top 0-2 inches. Approximately 25%, 52% and 65%, respectively, of the applied radiation remained in the top 0 to 2 inches. It was noted that triclopyr BEE was rapidly converted to triclopyr acid after application.

Attempts were made by Wauchope et al (1992) to estimate the Koc of triclopyr using data from published sources. The estimate of the Koc for triclopyr TEA was 20 L/Kg but this value was not considered to be particularly accurate because the published values have an extremely wide range. Similarly Ritter and Peacock (2000) estimated the Koc of triclopyr to be 53 L/Kg base on published values. These values are similar, and due to the extreme variation in the published values, these two estimates of Koc for triclopyr TEA are not significantly different from each other. Wuachope et al (1992) found the triclopyr BEE Koc to be 760 L/Kg, but in light of the values (Koc = ~50 L/Kg) found by Reeves for soil containing 1.1% to 2.7% organic carbon, this estimate appears to be excessively high. Since ticlopyr BEE is rapidly transformed to triclopyr acid, it is expected that the typical mobility for triclopyr acid is a more relevant value than that estimated for triclopyr BEE. Typically, the Koc for triclopyr acid would range from 31 to 422 L/Kg. In light of these values, triclopyr products would be considered to be mobile on most soils. But as discussed above, in the field, little evidence of triclopyr leaching has been found in soils. This is surprising since triclopyr is an organic acid that should be susceptible to leaching. This suggests that under-aged conditions or in the presence of large amounts of organic matter, that the leaching of triclopyr TEA, triclopyr BEE or triclopyr acid is unlikely (Branham, 1994).

Under aquatic field conditions, most of the triclopyr acid found in the system after application of triclopyr TEA at 2.5 ppm a.e. to control aquatic weeds remained in the water column or loosely associated with the sediment/water interface. In most systems, the concentration of triclopyr in the water column was 5- to 10-fold higher than in the sediment. This observation was true for most aging periods, which indicates that the concentration of triclopyr in water and sediment was an equilibrium process and adsorption was reversible. That is, both adsorption and desorption occurred readily (Getsinger et al, 2000; Petty et al, 1998; Woodburn et al, 1993; Green et al, 1989; Woodburn et al, 1988). In most field studies, complete dissipation of triclopyr and TCP occurs between 28 and 42 days. Under most situations, the applied triclopyr and its metabolites TCP and TMP will not be detectable at the end of the treatment season. It seems likely that the dissipation of triclopyr is primarily due to advection, dispersion and dilution in rivers and lakes (Getsinger et al, 2000; Petty et al, 1998; Getsinger et al, 1997 and Green et al, 1989) but may be primarily due to microbial metabolism and photolysis in ponds (Petty et al, 1998). However, in absence of light, the aerobic and anaerobic aquatic metabolism of triclopyr appears to be very slow in laboratory experiments (DT50 = 142 to 1300 days for aerobic and anaerobic aquatic metabolism, respectively) (EPA RED, 1998).

Adsorption of triclopyr to suspended sediment and algae (seston) is probably not significant. However, it has been noted that in some cases higher plant target species like Eurasian watermilfoil will bioconcentrate triclopyr at concentrations that are 10-fold higher than those seen in the water column. The amount of triclopyr released from these plants when they die is likely to be very low and therefore, this release is not likely to cause significant increases in the concentrations of triclopyr in the water column or sediment. For example, a related product (2,4-D) is accumulated in Eurasian watermilfoil at concentrations that may be 100-fold higher than those found in the water column. However, it was noted that the amount of 2,4-D released from dead or dying plant was only 1% of system total weight of 2,4-D (Birmingham and Colman, 1983 in Ebasco, 1993).

There are 22 degradates of triclopyr identified in Feng et al (1998) and Woodburn et al (1993). The metabolites TCP and TMP appear to be produced by direct microbial action on triclopyr acid. Photolysis or a combination of microbial metabolism and photolysis followed by additional microbial metabolism produces other metabolites. The ultimate products appear to be carbon dioxide, water and ammonium (after photolytic reductive dechlorination of triclopyr to a 2-ketopyridine followed by a photolytic ring opening to form 4-oxo-4-(amino)-2-buten-1-aldehyde). Another pathway exists where chlorine can be retained as the ring is photolyically cleaved into a 4-carbon straight chain alkene containing a triple-bonded nitrogen. From this point, a microbial degradation occurs to form $^{14}CO_2$, water and ammonium. However, the dichlordihydroxypyridines, which are intermediates of photolytic degradation cannot be degraded by a typical microbial organism [*Pseudomonas* sp. (ATCC 700113)]. In water, photolysis produces oxamic acid and 5-chloro-3,6-dihydroxy-2-pyridiny oxyacetic acid from triclopyr acid and (5/6)-chloro-3-hydroxy-s-pyridine from triclopyr BEE. Greater details on these degradative pathways can be found in Sections 3.2.4.3 and 3.2.6

In the EPA RED (1998) and in Larson, et al (1996), 379 wells were monitored and residues were found in only 5 wells in 2 separate states. Since a total of 379 wells were monitored and the highest concentration of triclopyr detected was <0.00058 ppm, triclopyr does not meet the detection trigger for recommending restricted use. Triclopyr acid has not been detected in well water in Washington State. Over 200 well sites were tested in various locations throughout the state including Lynden, Skagit Delta, East Chehalis, Woodland, Ahtanum, Gleed, Moxee, Sunnyside, Quincy, Pasco and Walla Walla.

In the State of Washington, triclopyr has been detected in the surface water of some small streams in the Puget Sound during 1987 to 1995. Numerous sites spread throughout the Puget Sound region have been monitored. Concentrations of triclopyr ranged from ~0.000006 to ~0.001 ppm which is much below levels likely to affect aquatic life acutely (5.6 ppm) or chronically (0.560 ppm) (USGS, 1997 and USGS, 1999). Sites that have been monitored include Fishtrap Creek, Joe Leary Slough, Big Indian Slough, Little Indian Slough, Canway Slough, Big Ditch Slough, Sullivan Slough, Swamp Creek, Thornton Creek, North Fork of Thornton Creek, South Fork of Thornton Creek, Juanita Creek, Lyon Creek, Lewis Creek, Sunset Creek, Longfellow Creek, Miller Creek, Des Moines Creek, Little Soos Creek, Rock Creek, Mercer Creek, Mercer Slough, Clear Creek, Chambers Creek, Clover Creek and Muck Creek. Because of the extremely low levels of triclopyr acid in well and surface water, the EPA does not currently have groundwater or surface water advisories for triclopyr or its main degradate (TCP). Also, because the level of triclopyr in groundwater is low, public water systems are not required to be sampled and analyzed for triclopyr.

It is possible, although unlikely, that wells drilled very close to a pond or lake shore could draw water directly from a water body so rapidly that any triclopyr present in the lake would not have a chance to be diluted, broken down, or adsorbed to soil/sediment or aquatic weeds. Much would depend on the treatment rate, soil type and porosity, the depth of the ground water table, the frequency and volume of pumping, and other hydrological parameters. Under a worst case scenario of sand/gravel sediment with little or no clay or silt, triclopyr would not adsorb and/or be degraded and could, with a very heavy and continuous pumping of water, contaminate the groundwater. However, there have been no credible reports of groundwater contamination above the MCLG (0.5 ppm a.e.) when triclopyr is used according to the label.

Many lake bottoms have fluffy, light (flocculent) sediments rather than a solid surface. The much larger amount of particle surface in these flocculent sediments greatly increases the likelihood of triclopyr adsorption compared with firm-surfaced sediment. However, organic matter itself may participate in only a minor way in the sorption of triclopyr. Triclopyr is most likely to sorb onto soils and sediments, which have high organic carbon content and a low pH, silty clay loams or other soil/sediments which contain high percentages of expandable clays and a large number of CEC sites. However, most review articles indicate that triclopyr does not readily adsorb to soils and sediments with the possible exception of high organic carbon content peaty soils and forest soils (Jotcham et al, 1989 and Stephenson et al, 1990).

3.7.2 Groundwater and Surface water

While triclopyr TEA and triclopyr BEE are the formulations used to control weeds, only triclopyr TEA will be registered for control of submerged/emerged aquatic and wetland weeds. Furthermore, triclopyr acid and its degradate TCP are the chemicals of concern in the ground water assessment since triclopyr TEA is rapidly dissociated to triclopyr acid and TCP is formed fairly rapidly from the microbial metabolism of triclopyr acid. Both triclopyr acid and TCP can be considered to be very mobile; K_{ads} is typically less than 1 for both triclopyr acid and TCP. Furthermore, triclopyr acid and TCP are fairly persistent. The half life of triclopyr acid in the water column ranges from less than 1 day in open water that is well mixed and slowly flowing to 3.5 to 7.5 days in water that is protected from the affects of flow (advection and dispersion). In sediment, triclopyr acid has a half-life that ranges from about half to about twice that found in water, but it is expected that the half-life of triclopyr in sediment will be similar to that found in water since it does not strongly adsorb to sediment and is easily desorbed. The half-life of TCP in water and sediment appears to be similar to that of triclopyr. Triclopyr has been seen to persist in pond water at concentrations that exeed the MCLG (0.5 ppm a.e.) for up to 3 or 4 weeks. TCP has been seen to persist in pond water at concentrations of 0.02 ppm one day after application.

Triclopyr applied to soil usually has a half-life of less than 3 weeks and this is considered to be insufficent to cause groundwater concern in most cases. However, triclopyr has been observed to have soil half-lives of 4 to 8 weeks on some grounds covered with native short grasses. Triclopyr salts were observed to have DT50s of 75 to 81 days on Oregon pastureland. Some laboratory work also inidcates a long triclopyr half-life (9 to 307 days) is likely in rice paddy surface soils incubated at low temperatures (15°C) and/or under water saturated conditions (water tension = 0 kPa). Surface soils incubated under high temperatures (30°C) and non-saturated conditions (water tension = 100 kPa) often yielded much shorter triclopyr half-lives (14 to 248 days). However, the correlation between incubation conditions and half-life are not very high (Table 3.2.4). Herbicides which have a half-life of less than 21 days may have the potenial to leach through soils.

The weight of evidence for both laboratory and field dissipation studies indicates that triclopyr and its metabolite TCP have properties and characteristics similar to pesticides known to leach into groundwater. Triclopyr, applied as triclopyr BEE and/or its degradates, are known to move through the soil profile in both agricultural and forest situations to depths of 45 to 90 cm. Pesticides that move to these depths have the potential to leach into ground water when the water table is shallow (EPA RED, 1998). It seems likely that triclopyr BEE and triclopyr TEA both readily form triclopyr acid after application to the soil. Therefore, these products will be similar in their leaching potential. However, other lysimeter studies (Reeves et al, 1995) and forest terrestrial dissipation studies (Stephenson et al, 1990) have shown that triclopyr, applied as triclopyr BEE, does not leach significantly. Less than 1% of the applied triclopyr leaches into the eluted water to depths of 3.4 feet during a 2-year lysimeter study and the concentrations of triclopyr and TCP were only 0.00007 ppm for both the herbicide and its metabolite. The majority of the recovered radiation remained in the top 12 inches of the soil within the lysimeter and the bulk of this radiation is permanently bound to the soil. Also, triclopyr does not leach significantly into the water of artificial ditch banks located 12 to 13 meters down slope at the bottom of slopes typical of forest contours (7° to 8°). The concentrations located in this "surface" water were very low (0.00001 to 0.00096 ppm a.e.) when applied to sand soils and clay soils containing high organic carbon levels (33.8 and 74.2%, respectively).

In addition to the above criterion, use patterns, application rate, timing of applications, potential acreage treated, depth to groundwater, soil types, hydraulic gradient and climate are evaluated as part of the triggering criteria. A pesticide may be recommended for restricted use for groundwater concerns if it exceeds one or more characteristics for each of the 3 factors (persistence, mobility and detection). The mobility and persistence triggers indicate that triclopyr and its TCP degradate may contaminate groundwater. The mobility values obtained for both triclopyr and TCP trigger a groundwater concern (Kd = 0.165 to 0.975 L/Kg for triclopyr and 0.53 to 1.95 L/Kg for TCP, exceed the trigger level of 5.0 L/Kg). Persistence under hydrolysis conditions (stable for both triclopyr TEA and TCP), field dissipation conditions (>3 weeks for TCP) and lab-derived aerobic soil conditions (>1 year for TCP) exceed the trigger levels for persistence. However, no significant concentrations of triclopyr were detected in groundwater sampled from 379 wells; only 5 wells, 1 in Texas and 4 in Virginia, contained detectable levels of triclopyr. These concentrations of triclopyr ranged from 0.000006 to 0.00058 ppm. Both the number and concentrations of triclopyr were low enough that the triggers were not exceeded and restricted use was not recommended. The proposed MCLG (0.5 ppm a.e.) and the lifetime health advisory (HAL = 0.350 ppm a.e.) for triclopyr are not exceeded in the well monitoring studies. Therefore, public well water supply sites are not currently required to analyze for triclopyr (EPA RED, 1998).

Until triclopyr was used for the control of aquatic weeds, the main source of surface water contamination was through accidental direct over-spray. Concentrations of triclopyr in forest streams remained low (0.023 to 0.025 ppm), 3 days after treatment. This is typical for lake scenarios at typical forest use rates. Under these conditions, the stream water was not directly treated. Sediment concentrations (0.011 to 0.014 ppm) were also seen to be low under these treatment conditions. Triclopyr, TCP and TMP were not detected at concentrations higher than the limit of detection (0.010 ppm). It is likely that this low level of contamination was due to drift and that surface water contamination is not a serious issue under these conditions (EPA RED, 1998).

In cases where ponds were directly over-sprayed with these high rates of triclopyr, the concentration was seen to be as high as ~2.0 ppm immediately after treatment and decreased to levels (0.492 to 0.776 ppm) that approximate the MCLG (0.5 ppm) within one week of application. Concentrations of triclopyr dropped to ~0.04 ppm after 4 weeks of dissipation and <0.01 ppm (detection limit) ppm at 3 to 8 months after treatment. In pond sediment, triclopyr concentrations were 0.467 to 0.830 ppm immediately after treatment, rising to 0.613 to 1.55 ppm at 3 days post-application, 0.369 to 1.22 ppm at 14 days post treatment and 0.27 to 0.334 ppm at 4 weeks post treatment (EPA RED, 1998).

When triclopyr is applied directly to water at 2.5 ppm to control aquatic weeds, the immediate concentration of triclopyr in the water column or in the sediment can be quite high. Initial concentrations are close to 2.5 ppm in the water column and can be as high as 0.68 ppm in the sediment for 3 days after application. Usually, the concentrations triclopyr in water and sediment dissipates rapidly and drop below the MCLG (0.5 ppm) in 1 to 21days (depending on water conditions). Extensive dissipation occurs in the sediment, and at many lake sites, the concentration of triclopyr in sediment drops to ≤0.1 ppm a.e. in approximately 1 day after treatment. However, at pond treatment sites, the concentrations of triclopyr may persist at concentrations of greater than 1.0 ppm for more than 1 week (Table 3.5). TCP concentrations can also be significant in some water bodies. However, TCP is usually not detected at significant concentrations in lake water or sediment, and concentrations greater than 0.025 ppm are rarely seen. Furthermore, the concentration of TCP in pond water and sediment are ~0.2 ppm during the first week and will be mostly eliminated (concentrations of TCP <0.08 ppm) within 14 to 42 days. The values presented here are just general trends and more exact values for specific water bodies may be found in Table 3.5.

For surface water ponds, a 21-day water use restriction is specified in the Garlon® 3A label. This time period was necessary in pond situations for the concentration of triclopyr to drop below the MCLG (0.5 ppm a.e.) and the HAL (0.350 ppm) (Table 3.5). Also modeling work by Ritter and Peacock (2000) indicates that a setback distance of up to 600 meters is necessary to allow the concentration of triclopyr to drop below the MCLG (0.5 ppm) in a 14 ha (~35 acre) water body treated with 2.5 ppm to control submerged plants. A somewhat lower setback distance (380 meter) is required when 1.48 ppm a.e. triclopyr is applied to a 14 ha water body to control emerged aquatic plants. The work of Petty et al (1998) at Lake Minnetonka and Getsinger et al (1997) at the Pend Oreille River indicates that these setback distances are reasonable. The setback distances presented here are for the worst case scenario. For setback distances specific to certain applications, the Garlon® 3A or Renovate® label should be consulted. The setback distances recommended by Ritter and Peacock are based on the aerobic aquatic half-lives seen in field studies conducted at Lake Minnetonka, MN, Lake Seminole, GA, California, Missouri and Texas ponds. These aerobic aquatic half-life values are base on the half-lives of triclopyr seen in the water column. The field data presented by Ritter and Peacock have been previously discussed and presented in Table 3.5

In the Sate of Washington, groundwater was monitored for triclopyr between 1988 and 1995, and no triclopyr was found at well sites in Lynden, Skagit Delta, East Chehalis, Woodland, Ahtanum, Gleed, Moxee, Sunnyside, Quincy, Pasco and Walla, Walla. For most tested pesticides over 200 well sites were monitored. A related herbicide with similar physical properties has been detected in 2 of the 242 sites monitored for picloram and the maximum concentration detected was 0.00007 ppm. (Larson, 1996).

In the State of Washington, triclopyr has been detected in the surface water of some small streams in the Puget Sound during the 1987 to 1995 time frame. A large number of sites spread throughout the Puget Sound region have been monitored. Concentrations of triclopyr ranged from ~0.000006 to ~0.001 ppm and this is much below the levels that are likely to acutely or chronically affect aquatic life (USGS, 1997 and USGS, 1999). Sites that have been monitored include Fishhtrap Creek, Joe Leary Slough, Big Indian Slough, Little Indian Slough, Canway Slough, Big Ditch Slough, Sullivan Slough, Swamp Creek, Thornton Creek, North Fork of Thornton Creek, South Fork of Thornton Creek, Juanita Creek, Lyon Creek, Lewis Creek, Sunset Creek, Longfellow Creek, Miller Creek, Des

Moines Creek, Little Soos Creek, Rock Creek, Mercer Creek, Mercer Slough, Clear Creek, Chambers Creek, Clover Creek and Muck Creek.

Because of the extremely low levels of triclopyr acid in well and surface water, the EPA does not currently have ground or surface water advisories for triclopyr or its main degradate (TCP). However, continued monitoring for triclopyr and TCP is necessary after the new labels for Renovate® and Garlon® 3A are issued. Wells and surface water bodies should be monitored to determine if the new labeled aquatic application of triclopyr is safe and remains below the MCLG (0.5 ppm a.e.) and HAL (0.35 ppm a.e.) for potable groundwater. Similar monitoring of surface water should be conducted to ascertain whether the water use restriction time periods of 120 days for irrigation, 21 days for use of potable water from treated ponds are adequate. Concentrations of triclopyr in water used for irrigation should be below the limit of detection (0.01 to 0.00004 ppm a.e. depending on method) and concentrations of triclopyr in potable water should be below the MCLG (0.5 ppm a.e.). The setback distances should also continue to be monitored to determine if any unusual situations may require an additional setback when compared with those indicated in the Garlon® 3A label.

Table 3.7
Triclopyr Adsorption/Desorption Constants

Soil/sediment type	% organic	CEC (meq/g)	pH	% Clay	% Silt	% Sand	Active Ingredient	Kd_{ads}[1] (L/Kg)	Koc_{ads} (L/Kg)	Freundlich K_{ads} (L/Kg)	Freundlich Koc_{ads} (L/Kg)	Kd_{des}[1] (L/Kg)	Koc_{des} (L/Kg	Freundlich K_{ads} (L/Kg)	Reference
Crowley Silt Loam (AR) with 0 to 4 cm depth	0.8% om[2] 0.46% oc[3]	0.19	6.9	19			Triclopyr acid			0.54[2]	117*				Johnson et al, 1995
Crowley Silt Clay Loam (AR) with 58 to 62 cm depth	0.7% om 0.41% oc	0.26	5.0	37			Triclopyr acid			1.73	422*				Johnson et al, 1995
Perry Silty Clay (AR) with 0 to 4 cm depth	1.0% om 0.58% oc	0.43	6.9	50			Triclopyr acid			0.76	131*				Johnson et al, 1995
Perry Silt Clay (AR) with 58 to 62 cm depth	0.5% om 0.29% oc	0.48	5.3	56			Triclopyr acid			0.9	310*				Johnson et al, 1995
Crowley Silt Loam (AR) with 0 to 4 cm depth	0.8% om 0.46% oc	0.19	5	19			Triclopyr acid	0.58	126*						Johnson et al, 1995
Crowley Silt Loam (AR) with 0 to 4 cm depth	0.8% om 0.46% oc	0.19	7	19			Triclopyr acid	0.23	50*						Johnson et al, 1995
Crowley Silt Clay Loam (AR) with 58 to 62 cm depth	0.7% om 0.41% oc	0.26	5	37			Triclopyr acid	0.59	144*						Johnson et al, 1995

Table 3.7
Triclopyr Adsorption/Desorption Constants (continued)

Soil/sediment type	% organic	CEC (meq/g)	pH	% Clay	% Silt	% Sand	Active Ingredient	Kd_{ads}^{1} (L/Kg)	Koc_{ads} (L/Kg)	Freundlich K_{ads} (L/Kg)	Freundlich Koc_{ads} (L/Kg)	Kd_{des}^{1} (L/Kg)	Koc_{des} (L/Kg	Freundlich K_{ads} (L/Kg)	Reference
Crowley Silt Clay Loam (AR) with 58 to 62 cm depth	0.7% om 0.41% oc	0.26	7	37			Triclopyr acid	0.08	106*						Johnson et al, 1995
Perry Silty Clay (AR) with 0 to 4 cm depth	1.0% om 0.58% oc	0.43	5	50			Triclopyr acid	0.61	105*						Johnson et al, 1995
Perry Silty Clay (AR) with 0 to 4 cm depth	1.0% om 0.58% oc	0.43	7	50			Triclopyr acid	0.18	31*						Johnson et al, 1995
Perry Silt Clay (AR) with 58 to 62 cm depth	0.5% om 0.29% oc	0.48	5	56			Triclopyr acid	0.51	175*						Johnson et al, 1995
Perry Silt Clay (AR) with 58 to 62 cm depth	0.5% om 0.29% oc	0.48	7	56			Triclopyr acid	0.12	41*						Johnson et al, 1995
Forrest Gleysol (Ontario)	1.4% om 0.81% oc	0.29	5.6	86	12	2	Triclopyr BEE	0.38 mean	47* mean						Jotcham et al, 1989
Forest Podzol (Ontario)	1.4% om 0.81% oc	0.04	5.5	0	6	94	Triclopyr BEE	0.34 mean	42*						Jotcham et al, 1989
Forest Luvisol (Ontario)	2.3% om 1.3% oc	0.08	5.3	18	43	39	Triclopyr BEE	0.97 mean	75*						Jotcham et al, 1989

Table 3.7
Triclopyr Adsorption/Desorption Constants (continued)

Soil/sediment type	% organic	CEC (meq/g)	pH	% Clay	% Silt	% Sand	Active Ingredient	Kd_{ads}^{1} (L/Kg)	Koc_{ads} (L/Kg)	Freundlich K_{ads} (L/Kg)	Freundlich Koc_{ads} (L/Kg)	Kd_{des}^{1} (L/Kg)	Koc_{des} (L/Kg	Freundlich K_{ads} (L/Kg)	Reference
Forest Organic Peaty (Ontario)	84% om 40.3% oc	1.48	5.9	n.r.^{3}	n.r.^{3}	n.r.^{3}	Triclopyr BEE	15.5 mean	38.5*						Jotcham et al, 1989
Hammond Surface (LA)	3.4% oc	n.r.^{3}	6.2	33.3	42.8	21.0	Triclopyr TEA	0.012 estimate	3.51* estimate						Abdelgehani, 1995 in Obenshain et al 1997
Hammond Subsurface (LA)	3.4% oc	n.r.^{3}	6.2	33.3	42.8	21.0	Triclopyr TEA	0.036 estimate	1.059* estimate						Abdelgehani, 1995 in Obenshain et al 1997
Speyer 2.2 Loamy Sand (Germany)	2.1% oc						Triclopyr BEE	0.88	42*						Reeves, 1995
Sandy Clay (Europe)	1.1% oc						Triclopyr BEE	0.45	41*						Reeves, 1995
Sandy Clay loam (Europe)	1.7% oc						Triclopyr BEE	1.01	59*						Reeves, 1995
Sandy Clay (Europe)	2.7% oc						Triclopyr BEE	1.32	49*						Reeves, 1995

Table 3.7
Triclopyr Adsorption/Desorption Constants (continued)

Soil/sediment type	% organic	CEC (meq/g)	pH	% Clay	% Silt	% Sand	Active Ingredient	Kd$_{ads}$[1] (L/Kg)	Koc$_{ads}$ (L/Kg)	Freundlich K$_{ads}$ (L/Kg)	Freundlich Koc$_{ads}$ (L/Kg)	Kd$_{des}$[1] (L/Kg)	Koc$_{des}$ (L/Kg	Freundlich K$_{ads}$ (L/Kg)	Reference
Kalkaka Sand (HI)	0.73% oc	n.r.[3]	5.0	4	8	88	Triclopyr acid			0.975	133[*]		0-days aging 1.17 15 days aging 2.31 30 days aging 2.50	161 317 343	Woodburn et al, 1988
Londo Sandy Loam (MI)	2.25% oc	n.r.[3]	7.5	10	20	70	Triclopyr acid			0.571	25[*]		0-days aging 0.71 15 days aging 1.67 30 days aging 1.95	32[*] 74[*] 87[*]	Woodburn et al, 1988

Table 3.7
Triclopyr Adsorption/Desorption Constants (continued)

Soil/sediment type	% organic	CEC (meq/g)	pH	% Clay	% Silt	% Sand	Active Ingredient	Kd_{ads}[1] (L/Kg)	Koc_{ads} (L/Kg)	Freun-dlich K_{ads} (L/Kg)	Freun-dlich Koc_{ads} (L/Kg)	Kd_{des}[1] (L/Kg)	Koc_{des} (L/Kg	Freun-dlich K_{ads} (L/Kg)	Reference
Commerce Silt Loam (CA)	0.67% oc	n.r.[3]	7.7	14	52	34	Triclopyr acid			0.165	25*		0-days aging 0 0.34 15 days aging 0.87 30 days aging 0.95	51* 130* 142*	Woodburn et al, 1988
Mahoun Clay Loam (MI)	1.38% oc	n.r.[3]	6.6	35	41	23	Triclopyr acid			0.733	53*		0-days aging 1.4 15 days aging 5.30 30 days aging 4.53	102* 384* 328*	Woodburn et al, 1988

Table 3.7
Triclopyr Adsorption/Desorption Constants (continued)

Soil/sediment type	% organic	CEC (meq/g)	pH	% Clay	% Silt	% Sand	Active Ingredient	Kd_{ads}[1] (L/Kg)	Koc_{ads} (L/Kg)	Freundlich K_{ads} (L/Kg)	Freundlich Koc_{ads} (L/Kg)	Kd_{des}[1] (L/Kg)	Koc_{des} (L/Kg	Freundlich K_{ads} (L/Kg)	Reference
Kalkaka Sand (HI)	0.73% oc	n.r.[3]	5.0	4	8	88	TCP						30 days aging 0.18	25*	Woodburn et al, 1988
Londo Sandy Loam (MI)	2.25% oc	n.r.[3]	7.5	10	20	70	TCP						30 days aging 0.33	14*	Woodburn et al, 1988
Commerce Silt Loam (CA)	0.67% oc	n.r.[3]	7.7	14	52	34	TCP						30 days aging 0.58	86*	Woodburn et al, 1988
Mahoun Clay Loam (MI)	1.38% oc	n.r.[3]	6.6	35	41	23	TCP						30 days aging 0.58	41*	Woodburn et al, 1988
Sand, Sandy Loam, Silt Loam and Clay Loam	n.r.[3]	n.r.[3]	n.r.[3]	n.r.[3]	n.r.[3]	n.r.[3]	TCP			0.53-1.95					EPA RED, 1998

* K_{oc} values calculated by this reviewer using the equation $K_{oc} = (K_d / \%\ organic\ carbon) \times 100$. See text.

[1] ads = adsorption, des = desorption

[2] % om = percent organic matter

[3] % oc = percent organic carbon = % om x 0.58

[4] n.r. = data not reported

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Supplemental Environmental Impact Statement
Assessments of Aquatic Herbicides

Triclopyr

Volume 5, Section 4

ENVIRONMENTAL EFFECTS

160 PAGES

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4.0 ENVIRONMENTAL EFFECTS ASSESSMENT – TRICLOPYR

Executive Summary: The information contained in this report was compiled from studies submitted to EPA by the sponsor, data found on various EPA web-sites, and the open literature on the toxicity of triclopyr TEA salt and triclopyr acid. Data collected included acute toxicity for the standard test species of microbes (algae and protists), plants, fish, free-swimming invertebrates and benthic (sediment-dwelling) invertebrates. Chronic toxicity data consists of early life-stage studies for fish and amphibians and life-cycle studies for free swimming invertebrates. No chronic toxicity data was collected for algae, plants or sediment organisms. Although chronic data was in short supply, since the half-life of triclopyr is very short (typically <4 days) in open public waterways and somewhat longer (<7.5 days) in impounded waterways, chronic risk assessments were not believed to be necessary to determine the safety of triclopyr for the biota. However, acute to chronic toxicity ratios based on the LC_{50}*/MATC were calculated to determine this ratio and its variability. An estimate of the chronic Maximum Allowable Toxic Concentration (MATC) was made based on the acute/chronic toxicity ratio for animal species, which have both acute and chronic data available. In order to supplement the data further, additional data were collected on species other than the standard test species. A risk assessment was conducted based on the procedures outlined in Urban and Cook (1986) and the procedures outlined in Campbell et al (2000). Urban and Cook state that if acute risk quotients (RQs) are less than 0.1 and chronic risk quotients are less than 1.0, the biota should be safe from the toxic effects of the tested pesticide with assurance that 95% of the tested biota will be protected. These values are respectively termed the acute and chronic levels of concern. The acute RQ is defined as the short-term expected environmental concentration (EEC) divided by the acute* EC_{50}*; and the chronic RQ is defined as the long-term EEC divided by the chronic MATC.*

Campbell et al (2000) did not use safety factors as described in Urban and Cook (1986) but felt that if the EEC is not higher than the LC_{50} *in more than 90% of the cases that safety to the biota should be sufficient. Judgement must be used to determine the best approach based on past experience and the need to provide extra protection to threatened, endangered or sensitive species, and species that are key elements in the food-web.*

Acute risk quotients are defined as the 4-day time weighted average of the Expected Environmental Effects Concentration (EEC) divided by the concentration of the herbicide that will cause mortality or an other observable end point in 50% of animals exposed in a standardized acute toxicity test (EC_{50} *or* LC_{50}*). These values are calculated from the most typical initial concentration of triclopyr applied directly to water for the control of submersed weeds (2.5 ppm a.e.), and concentrations applied as a direct over-spray for the control of emersed or floating weeds at 2 gallons formulation/acre into six inches of water (4.4 ppm a.e.) or for brush control sprayed at 2 to 3 gallons formulation/acre on sites adjacent to a water way (0.185 to 0.270 ppm a.e.). A worst case scenario is also assumed where these rates are sprayed directly over a shallow water body due to an accident or misadventure (4.4 ppm to 6.6 ppm a.e.); half-life may be considered to be an important element in calculating the EEC. However, since triclopyr appears to have similar toxicity (*LC_{50} *or* EC_{50}*s) at 24, 48, 72, 96 hours and 21 and 28 days, triclopyr is believed to lack chronicity and the maximum initial concentration may be more important in determining risk from triclopyr exposure. For triclopyr, the water dissipation half-life ranges from <0.5 to about 4 days in most open aquatic ecosystems. However, half-lives as long as 7.5 days have been seen in water impounds where there is only low inflow and*

outflow of water. In the most practical worst case scenario, an impounded farm pond with an initial concentration of 2.5 ppm a.e. triclopyr TEA, the longest half-life observed was 7.5 days (Foster, 1997). The more typical half-life under this worst case scenario was approximately 6.5 days. The most typical concentration (EEC) at zero time for triclopyr is considered to be 2.5 ppm a.e. However, the short term EEC for a typical exposure of 4 days, with a half-life of 4.0 to 7.5 days, would be the time weighted average of the concentrations occurring during this exposure period. These values have been calculated by CSI to be 1.8 to 2.1 ppm a.e. (or approximately 2.0 ppm a.e.). These values were validated by Foster et al (1997) at Elkgrove, California, Columbia, Missouri and Lewisville, Texas, which had 4-day concentrations of ~0.3 to ~1.5 ppm a.e. Chronic Risk Quotients are defined as the 28-day time weighted average for the Expected Environmental Effects Concentration (TWA-EEC) divided by the no observed effect concentration or maximum allowable toxic concentration (NOEC or MATC) for animals after exposure in a standardized chronic toxicity test. These values are calculated from typical day-0 concentrations of triclopyr (2.5 ppm a.e.) and a typical half-life of 4.0 to 7.5 days. The long-term EEC for triclopyr is estimated to be 0.41 to 0.89 ppm a.e. based on the time-weighted average of the concentrations experienced during a 28-day exposure to triclopyr TEA. These values have also been verified by Foster (1997) who found mean concentration averaging less than 0.52 ppm a.e. for all sampling times of 7 days or greater. Significantly shorter half-lives and lower EECs have been observed for Lake Minnetonka, Minnesota and Lake Seminole, Georgia. For example, the triclopyr half-life at Lake Minnetonka and Lake Seminole were 3.7 and 0.5 to 3.5 days, respectively, which yields a 4-day time weighted EECs of 1.75 and 0.45 to 1.73 ppm a.e. The 28-day TWA-EEC for these open water lakes were 0.47 and 0.06 to 0.45 ppm a.e. The work of Getsinger et al (2000) and Green et al, (1989) verify these results with 3- to 4-day observed concentrations of 2.2 and 0.03 to 0.29 ppm a.e., respectively. After 14 days of dissipation, the concentration of triclopyr TEA in the water column was 0.056 and <0.01 to 0.06 ppm a.e., respectively. This data indicates that while acute exposure is significant, chronic exposure is unlikely when triclopyr TEA is used to control aquatic and wetland weeds.

Triclopyr TEA products (Renovate® and Garlon® 3A Specialty Herbicides) have been shown in the field to affect various aquatic and wetland macrophytes (Section 1, Table 2 and Appendix 2). Algal species are not typically affected by triclopyr TEA. Various species of macrophytes found in the water column are affected by concentrations of triclopyr ranging from 0.75 ppm to 2.5 ppm a.e. Many of the emerged and floating species of macrophytes are affected by treatment rates of 2 gallons formulation/surface acre sprayed directly on emerged or floating foliage. The initial concentration of triclopyr found in the water after treatment will vary depending on the depth of the water column, the density of the treated weeds and the species of weeds being treated. Wetland associated broad leaf annual, perennial weeds and woody brush can be controlled with treatments of Renovate® or Garlon® 3A ranging from 2 to 3 gallons formulation/acre. Although algal blooms are often found in water that has been treated with triclopyr TEA, these blooms are generally not believed to be due to treatment with triclopyr TEA. Control plots and plots treated with triclopyr TEA normally have similar algal numbers and diversity. Algal species found in treated lakes and ponds include the green algae species Spirogyra *spp.,* Cladophora *spp.,* Mougeotia *spp.,* Volvox *spp.,* Closterium, *and* Scenedesmus *spp.; Charophytes like* Chara *spp. and blue-green algae such as* Anabaena *spp. However, after treatment the green algaes are often seen to dominate the water body although it is believed that this is due to water quality that favors green algal growth at the time triclopyr treatment typically occurs (Foster et al, 1997). Eurasian watermilfoil* *has been controlled in the field at concentrations of 2.5 ppm a.e. and purple loosestrife has been controlled at treatment rates of 6% Garlon® 3A formulation applied directly to purple loosestrife foliage (Houtman et al, 1997, Gardner and Grue, 1996). Removal of Eurasian watermilfoil improves the habitat for growth of many native species of aquatic plants like duckweed* (Lemna *spp.), pondweeds* (Potamogeton *spp.), coontail* (Ceratophyllum demersum), *southern naiad* (Najas guadalupensis), *American pondweed* (Elodea canadensis) *and water paspalum* (Paspalum fluitans) *(Houtman et al, 1997; Gardner and Grue, 1997 and Foster et al, 1997. Native species such as coontail, southern naiad, and American waterweed, are sometimes adversely impacted (reduced in numbers) shortly after treatment with higher use rates (2.5 ppm a.e.). However, it is not entirely clear whether these reductions in plant populations are due to the effects of normal seasonal variations or the direct effects of triclopyr TEA.*

Laboratory data indicate that triclopyr TEA is generally safe to non-target species of plants including Lemna gibba, Lemna minor *and various species of green algae, blue-green algae and diatoms. Risk assessments indicate that the level of concern (1.0) is not exceeded when these species are exposed to the maximum aquatic use rate (2.5 ppm a.e.) or to adjacent wetlands at rates of 6 to 9 lbs. a.e./acre (0.185 to 0.267 ppm a.e. according to EPA, RED, 1998). The risk quotient for the most sensitive species* (Skeletonema costatum) *is 0.65 (RQ = EEC/EC_{50} = 2.5 ppm a.e./3.8 ppm a.e.), which confirms the hardiness of most native species.*

As a further confirmation of the safety of triclopyr to sensitive plant and algae species, the risk assessment scheme promoted by Peterson et al (1994) indicates a moderate to potentially low risk for all species of algae. Peterson lists Lemna minor *as being at high risk from triclopyr TEA. No species are listed as being at very high risk from exposure to triclopyr TEA. However, since* Lemna minor *is not affected at the 50% level by concentrations that are near the maximum use rate of triclopyr TEA, it is unlikely that this species would be adversely impacted by the use of Renovate® or Garlon® 3Afor the control of aquatic or wetland weed species. Risk to non-target aquatic species may occur only under conditions where triclopyr TEA is not applied according to the label or is used to control floating or emergent weeds in very shallow water.*

- ***Summary of Triclopyr Effects on Aquatic Animals***

  For fish, the standard bioassay time is 96 hours. Triclopyr TEA has a low laboratory acute toxicity to fish (96-hour LC_{50} = 82 to 439 ppm a.e. for rainbow trout fry and fathead minnow fry, respectively). Even if a direct overspray to shallow water during wetland weed control occurs, fish populations should not be at risk from exposure to triclopyr. Under this scenario the acute level of concern (0.10) will not be exceeded (RQ = 0.08 = 6.6 ppm a.e./82 ppm). Even the salmonids, which are of special concern as a game fish, aesthetically, and as representatives of an endangered group, are not particularly sensitive to triclopyr; the lowest LC_{50}s are 82, 96, 112, 167 and 182 ppm a.e. for rainbow trout fry, chum salmon fry, sockeye salmon fry, Coho salmon fry and Chinook salmon fry, respectively.

  Limited field data with sentinel organisms (caged fish) indicates that rainbow trout adjacent to areas treated for control of purple loosestrife, bluegill sunfish, largemouth bass, and brown bullhead in water treated for Eurasian watermilfoil control were not adversely impacted by triclopyr TEA. Mortalities with these species *were due to decreases in the dissolved oxygen content of the water body (Gardner and Grue, 1996; Foster et al, 1997 and Houtman et al, 1997). Similar fish mortalities were seen in both treated and controlled water bodies. Where amphibian surveys were taken,* Rana pipiens *(adults and tadpoles) were common in both treatment and control ponds.*

Seawater challenge tests with salmon smolts were not performed. However, data indicate that at concentrations of ~200 ppm Garlon® 3A formulation, Coho salmon fry will be adversely affected. Fortunately, such high concentrations are not environmentally relevant. However, concentrations that were approximately half the LC_{50} *produced threshold changes in the behavior of rainbow trout while concentrations of twice the* LC_{50} *were necessary to produce a significant avoidance response (Morgan et al, 1991). Furthermore, concentrations at up to 80% of the acute* LC_{50} *had no impact on typical measures of physiological stress in Coho salmon, including no effects on the haematocrit, leucocrit, oxygen consumption, plasma glucose levels and plasma lactate levels (Janz et al, 1991). It is therefore unlikely that sub-lethal concentrations of triclopyr TEA will have a measurable short-term impact on salmonids.*

The octanol/water partition coefficient was less than <1.0 at normal physiological pH. Therefore, fish and shellfish are not expected to bioaccumulate triclopyr TEA (Bailey and Hopkins, 1987). Due to the low octanol/water partition coefficient bioconcentration studies have been waved for triclopyr TEA (EPA, RED, 1998). However, laboratory bioconcentration studies with bluegill sunfish indicate that the BCF is 0.052 in edible tissue and 0.93 in inedible tissue. The main residues seen in edible fish flesh were triclopyr (0.03 ppm a.e.), TCP (3,5,6-trichloro-2-pyridinol = 0.009 ppm) and TMP (2-methoxy-3,5,6-tirchloropyridine = 0.018 ppm) and an unidentified conjugate (Lickly and Murphy, 1987). A wide variety of fish have been observed to not bioaccumulate triclopyr and concentrations in edible fish tissue harvested from the field vary from <0.051 ppm a.e. at day one and subsequent days after treatment in fish taken from Lake Minnetonka, Minnesota to ≤0.1 ppm a.e. at day 1 and subsequent days in fish taken from Lake Seminole (Getsinger et al, 2000 and Green et al, 1989). Fish harvested from ponds have similar concentrations of triclopyr in their edible tissue as those harvested from lakes. For example, the concentration of triclopyr in edible fish tissue taken from ponds in California, Missouri and Texas were uniformly less than 0.1 ppm a.e. at all sampling times (Petty et al, 1998). Since the metabolite (TCP) of toxicological concern is also low in edible tissue (<0.1 ppm), it is not likely that spot treatments with triclopyr in large water bodies will have any significant impact on the fishery or the consumption of fish. Therefore, it is not necessary to have a fishing restriction after the application of triclopyr TEA.

Shellfish (crayfish and clams) tend to bioaccumulate triclopyr and TCP at levels somewhat higher than fish. The concentrations in freshwater clams and edible crayfish meat range up to 0.178 ppm a.e. at Lake Minnetonka and up to 4.87 ppm a.e. at Lake Seminole. It can take as long as 21 days for the concentrations of triclopyr in crayfish meat to dissipate below the proposed shellfish residue tolerance (0.2 ppm) and approximately 8 days for triclopyr in edible clam meat to drop below the proposed residue tolerance. However, levels of TCP are generally seen at concentrations <0.05 ppm over a 14-day period. Therefore, a shellfish restriction of up to 21 days may be necessary to avoid exposing the public to concentrations of *triclopyr that exceed the proposed shellfish residue tolerance. Laboratory work confirms the dissipation time of triclopyr from crayfish tail meat and hepatopancreas tissue. However, the maximum concentrations of triclopyr seen in crayfish tail meat (0.051 ppm a.e.) and hepatopancreas (1.3 ppm a.e.) was generally much lower than the concentrations found in the field (Barron et al, 1991).*

For invertebrates, the standard bioassay times vary from species to species. For most species, the standard bioassay time is 96 hours. However, for Daphnia magna, *and eastern oyster (*Crassostrea virginica*) embryos/larvae, the standard bioassay time is 48 hours. Triclopyr is not highly toxic to most invertebrates. For example, 96-hour* LC_{50}*s range from 41 ppm a.e. for* Crassostrea virginica *spat to >314 ppm a.e. for the fiddler crab (*Uca pugilator*); and the 48-hour* LC_{50} *ranges from ~22 ppm a.e. for eastern oyster embryo/larvae to 376 ppm a.e. for* Daphnia magna. *To conduct a standard risk assessment under the EPA's worst case scenario, the applied rate would be 2.5 ppm c.e. Since triclopyr TEA shows little or no chronicity, the EEC that should be used is 2.5 ppm. In this case the Risk Quotient is slightly greater than the level of concern at 0.1 for eastern oyster embryo/larvae (RQ = 0.11 =2.5 ppm a.e./22 ppm a.e.). Since this risk quotient just barely exceeds the acute level of concern, it is unlikely that serious adverse affects will occur for aquatic invertebrates. Current guidance indicates that treating triclopyr as a restricted use herbicide should allow for an additional level of safety where the risk quotient level of concern can be raised to 0.5. This approach would make the use of triclopyr acceptable when embryo/larval oysters are likely to be impacted. This should be a rare event since the application of triclopyr TEA to estuaries is prohibited by the experimental Renovate® label and by the proposed Garlon® 3A label. Furthermore, any triclopyr that is transported into the estuary should be greatly diluted from the inflow of the freshwater source and the tidal saltwater addition from the ocean.*

Field data indicate that triclopyr used for the control of Eurasian water milfoil and purple loosestrife should not impact aquatic macro-invertebrates in an adverse manner. No decrease in numbers or diversity of aquatic macro-invertebrates found in the field could be attributed to the direct affects of triclopyr. Invertebrates that are typically found in similar number in both treated and untreated plots include Amphipods, Diptera, Odonata, Gastropoda, Notonectidae, Haliplus *spp., Ephemeroptera, Lestidae,* Daphnia, *Cladocera, and Chaoboridae. Rises and falls in the populations of these invertebrates can generally be attributed to natural seasonal fluctuations (Gardner and Grue, 1997 and Foster et al, 1997).*

The chronic toxicity of triclopyr has not been extensively evaluated in studies that would currently fulfill EPA study guidelines. However, one early life-stage study and one life cycle study has been conducted with this test substance. Since little chronicity is exhibited when fish and aquatic invertebrates are exposed to triclopyr TEA, chronic toxicity caused by triclopyr is unlikely. The LC_{50}*s for 31-day chronic tests were >52 and <81 ppm a.e. In the worst case scenario typically used by the EPA, it is estimated that a 2.5 ppm a.e. application of triclopyr TEA would dissipate to a time weighted average of 1.1, 0.89 and 0.82 ppm a.e. in 21, 28 and 31 days, respectively. These levels of triclopyr were validated in field pond studies conducted by Foster et al (1987), who found that triclopyr applied at rates of 2.5 ppm a.e. dissipated to <0.25 ppm a.e. in approximately 21 days. Similar findings were seen by Houtman et al (1997) and Green et al (1989), who found that triclopyr dissipated to concentrations of less than 0.1 ppm a.e. in 14 days at Lake Seminole, Georgia and*

Lake Minnetonka, Minnesota. However, the acute to chronic ratio for fathead minnow is 2.1 to 4.2 (LC_{50}/MATC = 86 to 176 ppm a.e../41 ppm a.e). The most sensitive species of fish (rainbow trout) would have a predicted MATC of 27 ppm a.e. (82 ppm a.e./3.0) and this value is much greater than the TWA-EEC predicted 31 days after treatment of a water body (EEC = 0.82 ppm c.e). Therefore, even the most sensitive species of fish is unlikely to be adversely impacted by chronic exposure to triclopyr. Since the predicted MATC is higher than the maximum initial concentration of 2.5 ppm a.e., the reproduction and growth of even the most sensitive species is not likely to be adversely impacted by exposure to non-degrading triclopyr concentrations even where it does not degrade readily.

The experimental chronic toxicity (MATC) is 35 ppm c.e. for Daphnia magna*. Under the worst case scenario of an initial application of 2.5 ppm a.e., the time weighted average concentration of triclopyr would dissipate to 1.1, 0.89 and 0.82 ppm a.e. in 21, 28 or 35 days, respectively. Therefore, it is unlikely that this species would be exposed to concentrations that would impact its growth and reproduction (RQ = EEC/MATC = 1.1 ppm c.e./35 ppm = 0.03 in 21 days). There is not enough data to predict the MATC for other species. However, the acute to chronic ratio for* Daphnia magna *is 10.7 (LC_{50}/MATC = 376 ppm a.e./35 ppm a.e). The most sensitive species of invertebrate (*Crassostrea virginica *embryo/larvae) would have a predicted MATC of 2.1 ppm a.e. (22 ppm/10.7). These MATC values are high enough to yield a chronic Risk Quotient for* Crassostrea virginica *embryo/larvae that is lower than the chronic level of concern (1.0) if the time weighted EEC is used to generate the risk quotient (RQ = 1.1 ppm a.e./2.1 ppm c.e. =0.52). Therefore, the most sensitive invertebrate species tested is not likely to be adversely impacted from chronic exposure to triclopyr if one assumes that lack of chronicity is not an issue. If lack of chronicity is an issue, the chronic level of concern will be slightly exceeded (2.5 ppm a.e. / 2.1 ppm a.e. = 1.2). Under this scenario, the most sensitive species of invertebrate may be impacted by chronic exposure to triclopyr for the control of aquatic weeds. However, this appears to be a problem only with estuarine species and estuarine species are unlikely to be exposed to triclopyr TEA. The most sensitive freshwater species (*Procambarus clarki*) has a predicted MATC that is >10 ppm c.e., which is higher than the initial exposure concentration of 2.5 ppm a.e. Therefore, the reproduction and growth of freshwater invertebrate species should not be adversely impacted by exposure to triclopyr TEA. As discussed above, field studies have been conducted to show that aquatic macro-invertebrates are not affected in numbers, diversity or dominant species when exposed for up to 12 weeks in ponds located in California, Missouri and Texas (Foster et al, 1997).*

There have been arguments made that the presence of sediment will reduce the bioaccumulation and hence, the toxicity of triclopyr TEA when benthic invertebrates are present (Green et al, 1989). Therefore, it is possible that after oysters have become in-fauna they will not be significantly exposed to triclopyr TEA. It is also unlikely that oyster embryos/larvae will be significantly exposed to triclopyr since they are largely nektonic prior to their in-fauna stages. Furthermore, since the predicted chronic MATC (3.8 ppm a.e.) for oyster spats is somewhat higher than for embryo/larvae, it is not entirely clear if the long-term reproductive capacity of oysters would be adversely impacted by chronic exposure to triclopyr TEA.

Conclusion: Triclopyr will have no significant acute or chronic impact on fish or freshwater invertebrates when rates recommended on the label are used.

_Field studies support the risk assessment. Acute exposure of fish to triclopyr TEA in the field does not appear to adversely impact survival. Acute and Chronic exposure of freshwater invertebrates to triclopyr in the field does not appear to impact numbers, diversity or dominant species. There appears to be virtually no tendency for triclopyr TEA to bioaccumulate in fish or invertebrates when exposed from contact with water treated with triclopyr TEA. However, while the concentrations of triclopyr in edible fish tissue have not exceeded the proposed fish residue tolerance of 0.2 ppm a.e., concentrations of triclopyr in clams and crayfish have exceeded the proposed tolerance for up to 8 and 21 days, respectively. Irrigated crop studies have not been conducted with triclopyr TEA, and therefore a 120-day irrigation restriction is required when water bodies are treated with triclopyr TEA for the control of aquatic weeds. Triclopyr accumulates in target plants like Eurasian watermilfoil until the plant dies (three to seven days after application), at concentrations up to 19 ppm a.e. Triclopyr does not accumulate in non-susceptible non-target plants like flatstem pondweed, and maximum concentrations of ~1.5 to 3.2 ppm a.e. may be found in these non-target plants after 1-day post application. Concentrations of triclopyr in non-target plants are virtually eliminated 7 to 14 days post treatment. Release of triclopyr after the death of susceptible plants does not appear to impact concentrations of triclopyr found in the water column or the sediment. Several treatment rates are listed on the label. The label states that 0.75 to 2.5 ppm a.e. will control submerged aquatic macrophytes, including Eurasian watermilfoil (_Myriophyllum spicatum_), parrotfeather (_Myriophyllum aquaticum_),and pennywort (_Hydrocotyle _spp.). The 0.5 to 2 gallons formulation/acre = 1.5 to 6 lbs. a.e./acre treatment rate will control emerged and floating aquatic macrophytes including alligatorweed (_Alternanthera philoxeroides_), American lotus (_Nelumbo lutea_), waterhyacinth (_Eichhornia crassipes_), water lilies (_Nuphar _spp. and_ Nymphaea odorata_), and water primrose (_Ludwigia uruguayensis_). The 0.25 to 3 gallons of formulation = 0.75 to 9 lbs. a.e./acre treatment rate will control terrestrial weeds, broadleaf weeds and woody plants associated with wet lands. The label should be consulted for species on which efficacy is claimed. Many species of native aquatic plant are not significantly affected by the use of triclopyr to control noxious and invasive aquatic weeds. However, some species of native weed may be affected at higher treatment rates. Native species that may be affected at higher treatment rates include coontail (_Ceratophyllum demersum_), American waterweed (_Elodea canadensis_), and southern naiad (_Najas guadalupensis_). Native species that appear to be tolerant to triclopyr include rushes (_Scirpus _spp.) cattails (_Typha _spp.), water paspalum (_Paspalum flutans_), certain naiad species (_Najas _spp.) and flatstem pondweed (_Potamogeton zosteriformis_). Algal species including blue-green algae, green algae and diatoms are largely unaffected by triclopyr TEA. Some concern has been expressed that species that have not been pests in the past may become dominant after treatment with triclopyr due to their resistance to triclopyr, lack of competition with other weeds and algae or lack of long-term effectiveness. Triclopyr should not be used in attempts to control species of aquatic weeds that are not specified on the label. Although laboratory data indicates that triclopyr may be toxic to more sensitive species of estuarine mollusc (_Crassostrea virginica_), the freshwater invertebrate biota is not at risk from the proper use of triclopyr TEA._

4.0.1 Objective

The purpose of this section is to update the environmental toxicity data and to use this data to assess the potential risks to wildlife and the environment from using triclopyr TEA products (Garlon® 3A and Renovate® Specialty Herbicides). When wildlife is discussed, the organisms referred to include aquatic plants and animals, terrestrial plants and animals, and microorganisms including algae, bacteria, and fungi.

4.0.2. Study Approach

4.0.2.1 Information Compilation

In order to collect appropriate information regarding wildlife toxicology, several sources of information were used. As a primary and definitive source of data, reports submitted to the EPA Environmental Effects Branch by the registrant Dow AgroSciences to support the registrations and re-registration of triclopyr products were used. These submittals are considered to be definitive sources on the wildlife toxicology of triclopyr because the tests are conducted in an agreed upon design with agreed upon organisms. These organisms are considered to be good representatives or good surrogates for highly sensitive plants and animals. Other sources of acute and chronic toxicity data include literature searches with the Dialog Online Database for refereed journal articles and compilations of data in the form of literature reviews (EPA RED, 1998). Such literature reviews are a good source of information for older data. Similar compilations of EPA data were also searched such as EPA's Brian Database (1999) and EPA's ECOTOX Database (1999). These are online databases for retrieval of data submitted to support registration (Brian Database, 1999) and data from referred journals used as supplemental material to be used for risk assessment and evaluation (ECOTOX Database, 1999). Significant conflict was found in the toxicity values reported in original Dow AgroSciences' documents and the EPA RED (1998). The values in the EPA RED were often reported in terms of active ingredient. However, these same values were reported as being formulation equivalence or on as received basis in the original Dow AgroSciences' document. The Dow AgroSciences' documents were generally considered to be the definitive source documents.

The US EPA and Washington's Department of the Ecology (Ecology) use these data for the following evaluations:

- To establish acute toxicity levels of active ingredients to test organisms
- To compare toxicity information with measured or estimated pesticide residues in the environment in order to assess potential impacts to fish and wildlife
- To provide data which determine the need for precautionary label statements and permit requirements in order to minimize potential adverse effects to wildlife and aquatic organisms
- To indicate the need for further laboratory and field studies to support regulatory decisions

If an adverse impact is noted in the basic data, additional studies are conducted and evaluated to determine the effects of the product on sensitive species and sensitive stages of those species. These studies typically take the form of long term chronic, early life stage, reproductive effects and life-cycle effects. These studies take into account the toxicity of the product and compare that toxicity with expected environmental concentrations. If an adverse impact is noted at levels consistent with environmental concentrations, further “field” or laboratory work is necessary to evaluate the acute and chronic effects on different organisms.

4.0.2.2 Risk Assessment Methodology

Risk assessment is conducted in a manner similar to that described in EPA (1982), Brooks (1973 in Ebasco (1993), Ecology (1980,1989 and 1991/1992) and in Urban and Cook (1985). For assessment of acute risk, the LC_{50} is determined for a variety of organisms within a class (fish, aquatic invertebrates, algae, other aquatic and terrestrial plants, birds and mammals). The LC_{50} is the concentration at which 50% mortality is seen; the LD_{50} is the “oral” or “dermal” dose at which 50% mortality is seen. The relative toxicity of these values is determined in two ways: Item 1) The EPA has certain specific descriptive classifications for inter-chemical comparisons only and these classifications do not reflect actual environmental concentrations or hazards to the test species. For an example of these classifications, please see Table 1; Item 2) The Acute LC_{50} or LD_{50} is compared with the Expected Environmental Concentration or Expected Environmental Dose (EEC or EED). The Acute Risk Quotient (ARQ) is determined by dividing the Expected Environmental Concentration (4-day geometric mean or other appropriate evaluation of the EEC or EED) by the laboratory measured acute toxicity (4-day LC_{50}, LD_{50}). The ARQ is not based on values obtained for a single species, but is based on the most sensitive environmentally relevant species in a specific segment of the biota; e.g. algae, other microbes, macrophytes, fish, free-swimming aquatic invertebrates, or benthic organisms. If the ARQ is <0.1, the evaluated pesticide is generally considered to be safe to that segment of the biota for exposures of short duration. A short duration is generally defined as 4 or 5 days. However, many investigators believe that this is an excessively cautious approach and that if 90% of the species will not be affected at the 50% level by concentrations that are found in 90% of the treated water bodies, the product should be judged to be safe to aquatic organisms.

Similar calculations are used for an assessment of chronic risk. However, chronic risk is based on an exposure period of 7 or more days. Seven days exposure is considered to be a short-term chronic risk. Typically 21 to 90 days exposure is considered to be a long-term chronic risk. Short-term chronic risk involves the exposure of sac-fry to the toxic substance and long-term chronic risk involves the exposure of newly fertilized egg through free swimming and actively growing fry. For invertebrates, the chronic life-cycle test involves exposure of newborns through 21 to 28 days when the maximum number of F1 newborns will have been deposited. Dividing the 28-day EEC by No Observed Effect Concentration (NOEC) or the Maximum Acceptable Toxic Concentration (MATC) determines the Chronic Risk Quotient. The CRQ is not based on the values obtained for a single species but is based on the most sensitive environmentally relevant species in a specific segment of the biota; e.g. algae, other microbes, macrophytes, fish, free-swimming aquatic invertebrates, or benthic organisms. If the CRQ is <1.0, the evaluated pesticide is generally considered to be safe to that segment of the biota for exposures of chronic duration.

To determine how well acute toxicity can predict chronic toxicity, an acute (LC_{50})/ chronic MATC ratio) was evaluated for species that had both values available. This ratio was taken regardless of the quality of the data and then the quality was evaluated. If an individual ratio was an extreme outlier, it was discarded for the purposes of assessing the acute/chronic toxicity ratio. If extensive chronic data was not available, the acute to chronic ratio was used to estimate the chronic toxicity for species where the test had not been conducted.

4.1 TRICLOPYR

*Summary: Two registered products containing triclopyr are used for controlling aquatic weeds and algae in the State of Washington. Several triclopyr products are registered for use in Washington State including Cool Power® Selective Herbicide, Horsepower® Granular Weed Killer, Horsepower® Selective Herbicide, Horsepower® Spot Weed Killer, Turflon® II Amine, XRM-5302® Premium Granular Weed Killer, XRM-5302® Premium Selective Herbicide, XRM-5202® Premium Spot Weed Killer, Garlon® 4 Specialty Herbicide, Garlon® 3A Specialty Herbicide and Renovate® Specialty Herbicide. Riverdale Chemical distributes all of these herbicides except Garlon® 4, Garlon® 3A and Renovate®. None of the Riverdale Products are registered for aquatic use. Garlon® 4 and Garlon® 3A are manufactured and distributed by Dow AgroSciences but only Garlon® 3A has a proposed aquatic and wetland use. Renovate® is distributed by SEPRO Corporation and is currently used under an experimental label in Washington State. Triclopyr TEA products (Garlon® 3A and Renovate®) are used primarily for the control of Eurasian watermilfoil (*Myriophyllum spicatum*), waterhyacinth (*Eichhornia crassipes*), alligatorweed (*Alternanthera philoxeroides*), and purple loosestrife (*Lythrum salicaria*). Many other species of submerged, emerged and floating aquatic weeds may be controlled. Triclopyr TEA products also control various annual and perennial broadleaf weeds and woody brush plants that may be found in associated wetlands. For greater detail please see Section 1, Table 2 and Appendix 2. Many native species of aquatic plants including rushes (*Scirpus *spp.), cattails (*Typha *spp.) and flatstem pondweed (*Potamogeton zosteriformis*) may come to dominate a water body if noxious invasive species are removed by the use of triclopyr TEA. Other species of aquatic plants including (*Ceratophyllum demersum*), American waterweed (*Elodea canadensis*), and southern naiad *(Najas guadlupensis*) will also compete more effectively if noxious and invasive species are removed. However, these species are known to be susceptible to the effects of triclopyr TEA at higher use rates (2.5 ppm a.e.). Algal species including blue-green algae, green algae, diatoms and charophytes are generally not affected in the field by use of triclopyr at the maximum use rate. In order to write a label and determine if these products are safe to the biota, organisms with an extensive history of use in pesticide testing are evaluated by the registrant for their response to acute and chronic exposure. The most sensitive, easily cultured species are selected for testing. The most sensitive stages of any organism are usually those when rapid growth is occurring or the time of reproduction or shortly thereafter when eggs or newborn offspring are present. The most likely exposure route should also be selected to most closely mimic environmental reality.*

There are currently eleven registered formulations of triclopyr in the United States. While registering all eleven formulations, Washington State is only likely to permit the use of Garlon® 3A and Renovate® for use in public waterways. These products contain triclopyr TEA containing 31.8% triclopyr acid equivalence (a.e.) [44.4 % triclopyr TEA]. This review directly addresses only these formulations with experimental or proposed labels for aquatic use in public waterways that have been proposed for registration in Washington State by the Washington State Department of Ecology and Washington State Department of Agriculture as of October 2000. The toxicity of triclopyr TEA in triclopyr acid equivalence will be addressed to support the risk assessment. It is the conjugate base of triclopyr that is effective against aquatic weeds and the acid itself is believed to be somewhat more toxic than the conjugate base. Since the pKa of triclopyr acid is ~2.68, it is unlikely that triclopyr will be encountered by aquatic organisms in its acid form. However, the conjugate base is likely to be encountered by aquatic organisms due to the dissociation of triclopyr TEA into the conjugate base and TEA. When triclopyr TEA was originally proposed for aquatic use, it became quickly apparent that when adsorbed by fish or domestic animals it was eliminated largely unchanged (22 to >80 % triclopyr) from the organism, although the presence of small amounts (<10% of the recovered residue) of TCP (which is of toxicological concern) were found. The concentration of triclopyr plus TCP does not exceed the proposed fish residue tolerance of 0.2 ppm a.e. (Lickly, and Murphy, 1987 and Green et al, 1989). However, the concentration of triclopyr in clams and crayfish may exceed the proposed shellfish residue tolerance (0.2 ppm a.e.) for up to 8 and 21 days, respectively.

The triclopyr products currently registered for aquatic and wetland use in Washington State are as follows:

Garlon® 3A Specialty Herbicide -- A liquid product containing 44.4% triclopyr TEA (31.8% triclopyr acid = 3.0 lbs a.e./gallon). Manufactured and distributed by Dow AgroSciences. Labeled for use in ponds, lakes, reservoirs and marshes as well as their adjacent banks and shores. It may also be used in non-irrigation ditches and canals, which have little or no continuous outflow. The product may also be applied to wetlands that occur within forests, non-crop sites, wildlife habitat restoration and management areas. Also included in the meaning of wetlands are areas adjacent to and surrounding domestic water supply reservoirs, lakes and ponds.

Renovate® Specialty Herbicide -- A liquid product containing 44.4% triclopyr TEA (31.8% triclopyr acid = 3.0 lbs a.e./gallon). Manufactured by Dow AgroSciences and distributed by SEPRO Corporation. Labeled for application in ponds, lakes, reservoirs and marshes as well as their adjacent banks and shores. It may also be used in non-irrigation ditches and canals, which have little or no continuous outflow. The product may also be applied to wetlands that occur within forests, non-crop sites, wildlife habitat restoration and management areas. Also included in the meaning of wetlands are areas adjacent to and surrounding domestic water supply reservoirs, lakes and ponds.

Although there are a wide range of other triclopyr products available for use, only Garlon® 3A and Renovate® appear to be proposed for labeled use in public waterways.

Currently, triclopyr TEA (Garlon® 3A and Renovate®) only has an experimental label and a proposed label. See Section 1, Appendix 1 and 2 for examples of these experimental and proposed labels. These liquid formulations contain 44.4% triclopyr TEA (31.8% triclopyr acid = 3 lbs a.e./gallon). This product has been used experimentally in Washington to control Eurasian watermilfoil (*Myriophyllum spicatum*) and purple loosestrife (*Lythrum salicaria*). The proposed label also claims efficacy against floating aquatic species like waterhyacinth (*Eichhornia crassipes*), emerged species like alligatorweed (*Alternanthera philoxeroides*), American lotus (*Nelumbo lutea*), water lilies (*Nuphar* spp. and *Nymphaea odorata*) and waterprimrose (*Ludwigia uruguayensis*), and submerged species like Eurasian watermilfoil, parrotsfeather (*Myriophyllum aquaticum*) and pennywort (*Hydrocotyle* spp.). Furthermore, the proposed label claims efficacy on a variety of annual and perennial broadleaf weeds and woody brush that are discussed in Section 1 (Table 2 and Appendix 1 and 2). Species that will probably not be controlled at most typical rates of application include blue-green algae, green algae, diatoms, and Charophytes as well as certain native macrophytes like coontail (*Ceratophyllum demersum*), flatstem pondweed (*Potamogeton zosteriformis*), American waterweed (*Elodea canadensis*), southern naiad (*Najas guadalupensis*) and water paspalum (*Paspalum fluitans*). Removal of Eurasian watermilfoil will generally allow the native species of aquatic plants to compete more effectively for aquatic habitat (Houtman et al, 1997; Foster et al, 1997 and Petty et al, 1998).

4.1.1 Evaluated Organisms and Sensitive Stages (EPA, 1982)

In order to develop the most sensitive risk assessment possible, appropriate species and appropriate life stages must be chosen within each class of organisms. The classes of organisms of interest are microorganisms (bacteria, fungi and algae), macrophytes, fish, aquatic invertebrates, sediment organisms (includes several classes), terrestrial plants, birds, mammals and terrestrial invertebrates (includes several classes). The life-stages that are tested are selected for high sensitivity and ease of manipulation. Each class of organism is broken down into appropriate species as indicated in Table 2.

- **Microbes --** Very little work has been conducted on microbes, particularly aquatic bacteria and fungi. Although most authors cite photolysis and bacterial degradation as the primary route of degradation for triclopyr TEA, no authors have cited specific works on the degradation of triclopyr by bacteria or the affects of triclopyr on bacteria and other microbes.

- **Algae --** There are four standard species that are typically evaluated in algal toxicity tests. They are *Anabaena flos-aquae* (freshwater blue-green algae), *Selenastrum capricornutum* (freshwater green algae), *Navicula pelliculosa* (freshwater diatom) and *Skeletonema costatum* (marine diatom). These have been selected as the standard species because there is an extensive database on the effects of many pesticides on their growth rate. An additional algal species, *Ankistrodresmus* spp. has been evaluated for the toxic effects of triclopyr TEA. In general, triclopyr is not expected to have adverse impact on algal species when used according to the Renovate® and Garlon® 3A labels. The endpoint of interest in algal studies is a 50% reduction in log-phase growth after five days of exposure to a static solution (EC_{50}). Field studies normally measure the amount of chlorophyll a or use cell counts at the site as an indicator of population size.

- **Aquatic macrophytes --** For macrophytes, one genus (*Lemna gibba* and *Lemna minor* or duckweeds) is typically used in the laboratory. Duckweed is a standard genus with an extensive database on the effects of many pesticides on its growth rate. Results from the standard test species were reported to EPA and it is the only species with extensive laboratory work conducted on it. However, additional laboratory work has been conducted on Eurasian watermilfoil to determine the efficacy of triclopyr TEA.

- **Fish toxicity**

  Acute toxicity: The standard species tested in the laboratory include *Oncorhynchus mykiss* (rainbow trout), *Lepomis macrochirus* (bluegill sunfish), *Pimephales promelas* (fathead minnow), *Cyprinodon variegatus* (sheepshead minnow), and *Ictalurus punctatus* (channel catfish). Rainbow trout, bluegill sunfish, fathead minnow, and several species of salmon (*Oncorhynchus* spp.) were tested with triclopyr TEA. Rainbow trout, chum salmon, Coho salmon, sockeye salmon, pink salmon, and Chinook salmon are representatives of the cold water species (salmonids) requirement, and the warm water species requirement is fulfilled by tests with bluegill sunfish and fathead minnow. The marine and estuarine species requirement would be fulfilled by tests with the tidewater silverside (*Menidia beryllina*). The standard acute LC_{50} test is run with juvenile fish of a uniform age-class or size, which would typically fall in the class of fingerling (<0.5 grams). These acute toxicity tests are not typically run with smolts, eggs and sac-fry, but in some cases acute toxicity information is provided for these stages. The test is typically run for 96 hours, although some of the LC_{50}s may be based on 24-, 48- or 120-hour mortality data. The measured endpoint is mortality. The species selected are considered to be representative of a broad sensitivity range and ecological, economic and aesthetic relevance. Other species may also be tested. Those of particular interest based on ecological relevance and/or sensitivity to pesticides are striped bass (*Morone saxatilis*), largemouth bass (Micropterus salmoides), smallmouth bass (*M. dolomieu*), walleye (*Stizostedion vitreu*), and various salmonids (*Onchorhynchus* spp. and *Salmo* spp.). No recognized work has been done with most of these species using triclopyr TEA.

  Chronic toxicity: The standard species tested for chronic toxicity are fathead minnows, rainbow trout, and sheepshead minnow or tidewater silverside which represent a warm freshwater species, a cold freshwater species, and warm estuarine species. Consensus opinion is that rainbow trout are the most sensitive species in this group. Chronic toxicity tests can be run in the sac-fry stage for at least 7 days (standard time period, 28 days). In addition to mortality, the endpoints are growth and sub-lethal behavioral effects. Another study design is the early life-stage test where the endpoints are percent hatch, time to first and last (95%) hatch, swim-up or first-feed, growth and sub-lethal behavioral effects. The effective concentration is the lowest NOEC value obtained for the most sensitive endpoint. In summary reports that are obtained from agencies or registrants, the most sensitive endpoint is often not expressed. In some reporting formats, the effective concentration may be termed the No Observed Effect Concentration (NOEC), Lowest Observed Effect Concentration (LOEC) or the Maximum Allowable Toxic Concentration (MATC), which is the geometric mean of the NOEC and the LOEC. This is a very sensitive test and it often may yield an unacceptably high CRQ when the ARQ indicates a high degree of safety for the more sensitive species in the biota. When endpoints other than survival are used, the MATC is considered to be the concentration of interest for performing risk assessment. For triclopyr TEA, only the test with fathead minnow was considered adequate for risk assessment purposes. No chronic tests with cold water species have been run with either triclopyr TEA or its “toxic” and persistent metabolite TCP. It may be advisable to run chronic toxicity tests with triclopyr TEA and TCP against rainbow trout or another salmonid.

- **Aquatic invertebrates**

  - **Acute aquatic invertebrate toxicity:** For aquatic invertebrates, the standard species tested for acute toxicity include *Daphnia magna* (water flea), *Ceriodaphnia dubia* (water flea), *Mysidopsis bahia* (pocket shrimp) and *Crassostrea virginica* (eastern oyster), which represent two warm freshwater species and two warm estuarine species. Consensus opinion is that the eastern oyster test is usually the most sensitive. Only two of these species have been tested with triclopyr; *Daphnia magna*, and the eastern oyster. The endpoints for these tests are immobility for the arthropod species and shell growth for the eastern oyster. The endpoint is expressed as the 48- or 96-hour EC_{50} or LC_{50} for the three arthropods causing immobility or mortality, and EC_{50} (dosage causing 50% decrease in shell growth in 96 hours) for the oyster. In addition to these tests an embryo/larvae eastern oyster test has been conducted. However, the extreme sensitivity and environmental relevance of the embryo/larvae oyster test has been questioned particularly for compounds like triclopyr TEA, which are prohibited from use in the estuarine environment. Furthermore, since embryo/larvae oysters spend most of their time before in-faunal stages as a nektonic species, the relevance of using this stage as an indicator of environmental sensitivity is questionable. A number of other non-standard species and non-standard methods were tested with the triclopyr TEA and are listed along with a summary of the data in Table 2.

  - **Life-Cycle invertebrate toxicity:** Life-cycle invertebrate toxicity studies are typically done with *Daphnia magna* (daphnia), *Ceriodaphnia dubia* (daphnia) and *Mysidopsis bahia* (mysid shrimp). However, a very limited database is available for triclopyr products and their chronic effects on invertebrates. The only species of invertebrate that has been tested with triclopyr is *Daphnia magna*. Since this is the only life-cycle test presented, the database may be insufficient to support life-cycle safety of triclopyr on invertebrates. These tests are usually run for 21 days with *Daphnia magna*, 7 days with *Ceriodaphnia dubia* and 28 days with mysid shrimp. The parent generation is selected from a group of animals less than 24 hours old. The endpoints are immobility, reduction in number of live newborns produced per female, and growth of the parent daphnids or mysids during the test. The endpoint is expressed as the most sensitive EC_{50} in reference to immobility, reduction in neonate production and reduction in growth and the NOEC or MATC in reference to the most sensitive endpoint. The advantage of using the mysid shrimp, as a test organism is that, since it shows sexual dimorphism, certain endocrine disruptive effects could be determined in the parental generation as it matures. However, these endocrine effects cannot be interpreted or correlated with similar effects on vertebrates since it is unlikely that the effects of steroid sex hormones like estrogen or testosterone determine sex in this species. However, this species was not tested for triclopyr's effect on its life-cycle.

- **Sediment organisms**

  Sediment organism acute toxicity: There are major disagreements among scientists as to how sediment organism studies should be conducted. The disagreements are so great that many researchers believe daphnia studies make good surrogates for sediment organism studies. The main problem with sediment organism studies is that these organisms require sediment with a specific particle size in order to function properly in a physiological sense. However, in acute tests the sediment is often eliminated from the study because it adsorbs the toxicant and interferes with analytical chemistry when the sediment phase must be extracted. Most short-term (acute) 96-hour sediment organism studies are conducted without sediment present. There is a need for these tests since there is no reason to assume that sediment organisms will respond in a manner similar to other aquatic invertebrates. These sediment organism acute toxicity studies are conducted in a similar manner as acute tests with other invertebrates except that the age at initial exposure and the exposure period is specific to each species. These specific characteristics are listed in Table 2. However, since triclopyr TEA is generally not bound to sediments (Woodburn et al, 1988), the presence of sediment is unlikely to affect the toxicity of benthic organisms that occupy the surface of the benthos. However, benthic in-faunal species may be protected from adsorption of triclopyr (Green et al, 1989) since after soil adsorption occurs, the tendency of aged triclopyr to desorb is quite low (Woodburn et al, 1988).

4.1.2 Exposure Routes

Regardless of the organism, aquatic exposure to triclopyr can take several routes. These include adsorption from the water column, consumption of water or organisms while eating, contact with plants or sediments that have been treated with the test substance, or eating the granules. More detail for exposure routes is given below:

- Aquatic Algae and Plants: Exposure is through adsorption from the water column.
- Fish and Aquatic Invertebrates: Fish and aquatic invertebrates can be exposed to triclopyr by:
  - Adsorption through the “skin” or cuticle.
  - Adsorption through the gills.
  - Adsorption through the gut from the consumption of other animals or plant and algal material.
  - Adsorption through the gut after eating the formulated pesticide granules found at the bottom of the water body. This is not relevant to triclopyr since the formulation of triclopyr typically used is a liquid.
  - Detritovoirs can be exposed through eating detritus found in the sediment or catching the detritus from upper regions as it floats past.

For terrestrial organisms, exposure routes can be: 1) contact with treated water, 2) consumption of treated water, 3) consumption of organisms that have been in treated water, or 4) consumption of the pesticide granules if they have access to them; again not relevant to triclopyr liquid formulations.

4.2 ENVIRONMENTAL TOXICITY REVIEW: EFFECTS OF THE PHYSICAL AND CHEMICAL ENVIRONMENT ON HABITAT

There is no evidence that prior exposure to triclopyr will enhance the degradation of triclopyr by microbial organisms. It has been reported that the main route of triclopyr degradation is photolysis to TCP [the photolysis product (5-chloro-3,6-dihydroxy-2-pyridinyl acetic acid)] with 48% of the applied triclopyr degrading to the photolysis product and 16% of the applied triclopyr degrading to oxamic acid (EPA, RED, 1998). The photolysis half-life in pH 7 water is 0.6 days using natural light. Indications are that triclopyr and its photolysis products is also degraded by bacteria and other aquatic microbes found under aerobic and anaerobic conditions, to TCP (3,5,6-trichloro-2-pyridinol), TMP (3,5,6-trichloro-2-meththoxypyridine), carbon dioxide, water and various organic acids (Woodburn and Caranor, 1987 in Getsinger et al, 2000). Both laboratory and field data indicate that triclopyr and TCP are removed from the water column by sorption to the soil at only minimal levels. When triclopyr TEA was applied in the field at 2.5 ppm a.e., concentrations of triclopyr found in the sediment were at maximum concentrations of 0.257 to 0.334 ppm a.e. in Lake Minnetonka, Minnesota, <0.1 to 0.64 in Lake Seminole, Georgia, 0.388 to 0.860 ppm in a pond in Elk Grove, California, 0.080 to 0.173 ppm a.e. in a pond in Columbia, Missouri and 0.264 to 0.453 ppm a.e. in a pond in Lewisville, Texas. The maximum concentrations of the toxic metabolite (TCP) in sediment does not exceed 0.134 ppm a.e. at any of the monitored sites. The sediment half-life for triclopyr at these sites ranged from 2.8 to 5.0 days and complete dissipation to concentrations <0.01 ppm a.e. generally occurred within one day to four weeks. The toxic metabolite (TCP) is somewhat more persistent than triclopyr with a half-life of 3.8 to 13.3 days and complete dissipation to concentrations of <0.01 ppm within one day to 12 weeks (Getsinger et al, 2000, Petty et al , 1998 and Green et al, 1989).

Triclopyr does not readily bind to soil (Kd = 0.165 to 0.975 mL/g). Such a low adsorption coefficient indicates that there is potential for triclopyr to leach into the ground water. However, of the 379 wells sampled for ground water contamination by triclopyr in the United States, there have been only five detections at concentrations of <0.00058 ppm a.e. Therefore, while triclopyr exceeds the mobility and persistence triggers used to recommend restricted use, triclopyr does not meet detection triggers for recommending restricted use due to limited monitoring data (Hoheisel et al, 1992 in EPA RED, 1998). Since the toxic metabolite of triclopyr is considered to be persistent in water (t1/2 > 4-days) and may occur at concentrations of >0.01 ppm, a freshwater fish early life-stage study must be conducted using the most sensitive species of fish (rainbow trout).

Triclopyr is persistent in water (t1/2 =0.5 to 7.5 days) and exceeds the trigger concentration of 0.01 ppm a.e. Therefore, a fish early life-stage study is required (Getsinger, et al, 2000, EPA RED, 1998; Petty et al, 1998 and Green et al, 1989). However, since the acute toxicity of triclopyr TEA to rainbow trout and fathead minnow are approximately the same (82 and 86 ppm a.e., respectively), the fathead minnow early life-stage study is adequate for the early life-stage study requirement (EPA RED, 1998).

Other active ingredients for aquatic weed control that are typically used in Washington State may have water half-lives that are significantly less than triclopyr TEA. For example, the water half-lives for endothall (~0.8 days) and diquat (~0.75 days) are much less than that for triclopyr (t1/2 = 0.5 to 7.5 days). Short observed half-lives for triclopyr are generally correlated with waterways that are more open and have a greater flow rate. Longer observed half-lives appear to be associated with less open waterways or ponds with little or no outward flow.

Triclopyr does not adsorb extensively to sediment, fish, shellfish or plants. However, adsorption to plants is relatively high in target species and can reach concentrations as high as 19 ppm a.e. (BCF = ~10); but remains low <1.4 to 3.2 ppm a.e. (BCF = 0.53 to 1.4) on non-target plants like *Potamogeton zosteriformis*. Release of triclopyr to the water column is unlikely to be high enough to cause adverse impact on the remaining aquatic macrophytes. For example, native plant species such as *Najas guadlupensis*, *N. minor*, *Potamogeton nodosus*, *P. crispus, P. zosteriformis*, other native pondweed species (*Potamogeton* spp.), *Elodea canadensis*, and *Heteranthera dubia* and *Ranunculus longirostris* have often shown no evidence of injury after treatment with triclopyr TEA to control Eurasian watermilfoil in waterways which have reasonable rates of flow like the Pend Oreille River, Lake Minnetonka or Lake Seminole (Netherland and Getsinger, 1993 and Getsinger et al, 1997). However, higher treatment rates of 2.5 ppm a.e. used to control weeds in impounded water situations may damage more sensitive species. Triclopyr dissipates in water to levels below the detectable limit of ~0.01 ppm in approximately 4 to 6 weeks in water impounds (ponds) where the whole pond was treated (Petty et al, 1998) but complete dissipation can occur in less than three days at sites that are spot treated [(Lake Seminole, Georgia) Green et al, 1989)]. Even at the maximum use rate for controlling submersed aquatic weeds (2.5 ppm a.e.) or at concentrations used to control floating or emergent aquatic weeds (6 lbs a.e./ha = 0.37 to 4.4 ppm a.e.), the initial concentrations are unlikely to harm fish and, if used as a restricted use herbicide, damage to the most sensitive estuarine invertebrate (mollusc species) is unlikely since the LC_{50} for the most sensitive fish and invertebrates is 82 and 22 ppm a.e., respectively.

Bioconcentration in plants only occurs at a very low level. Concentrations in submersed aquatic plants have been seen to be as high as 19.1 a.e. ppm (BCF= ~10) in Eurasian watermilfoil 3 days after treatment of Lake Minnetonka to control this species at 2.5 ppm a.e. triclopyr TEA. However, stands of *Hydrilla verticillata* and *Myriophyllum spicatum* were found to contain from 6.5 to 10.5 ppm a.e. (BCF = ~2.6 to 4.2) triclopyr TEA on the day of treatment but were found to have dissipated to below detection levels in 8 to 14 days after treatment with 2.5 ppm a.e. at the Lake Seminole site. The non-target species (*Potamogeton zosteriformis*) do not readily accumulate triclopyr TEA from the water column. *Potamogeton zosteriformis* adsorbs triclopyr TEA [1.5 to 3.2 ppm a.e. (BCF = 0.5 to 2.2)] on the day of treatment but largely eliminates triclopyr [0.220 to 0.443 ppm a.e. (BCF = 0.5 to 0.31)] by the 7th day after treatment. Bioconcentration in animals has not been seen with triclopyr.

Whole body bioconcentration factors are less than one for bluegill sunfish (Lickly and Murphy, 1987). In the field, the highest concentration of triclopyr in edible fish flesh after treatment with 2.5 ppm a.e. triclopyr is TEA <0.2 ppm a.e. and typically ranges between<0.01 to 0.061 ppm a.e.; there does not seem to be a significant difference in the levels of triclopyr in game and non-game fish (Getsinger et al 2000; Petty et al, 1998 and Green et al, 1989). These concentrations are below the proposed fish residue tolerance of 0.2 ppm a.e. triclopyr. The maximum concentration of the toxic metabolite (TCP is also low with concentrations of TCP ranging from <0.01 to 0.07 ppm. Therefore, adverse impact on the fishery would not be expected when triclopyr is used to control aquatic weeds.

The BCF was somewhat greater than 1.0 in crayfish and freshwater clams. The maximum concentration of triclopyr found in crayfish was 0.178 to 4.87 ppm a.e. It could take up to 21 days for crayfish to dissipate triclopyr below the proposed 0.2 ppm a.e. residue tolerance for shellfish. Concentrations of triclopyr in freshwater clams could be as high as 2.49 ppm a.e., which is also above the proposed shellfish residue tolerance. It may take up to 8 days for clams to dissipate triclopyr to levels below the shellfish residue tolerance. Concentrations of the toxic metabolite (TCP) can be as high as 0.49 ppm a.e. in crayfish and 0.06 ppm a.e. in fresh water clams. However, concentrations of this metabolite fall below detectable limits in 21 and 8 days for crayfish and freshwater clams, respectively. More work may be necessary to establish a shellfish tolerance since the potential for adverse impact on shellfish fisheries is not entirely understood (Getsinger et al, 2000 and Green et al, 1989).

4.2.1 Potential Soil and Sediment Interactions

4.2.1.1 Impact of Various Soils (Sediment/Substrate) Composition

Summary: Due to its extremely low soil/water distribution coefficient, triclopyr adsorbs poorly to most soils. The adsorption coefficient ranges between 0.165 to 0.975 mL/g. These very low soil/water distribution coefficients make it unlikely that sediment will participate to any extensive degree in removing triclopyr TEA from the water column (Woodburn et al, 1988). Therefore, the concentration of triclopyr in sediment is usually quite low with the highest concentrations typically ranging from 0.21 to 0.86 ppm a.e. However, triclopyr typically disappears from the sediment in 1 day to 4 weeks. More rapid dissipation from the sediment occurs in open water bodies that have extensive water exchange, while longer dissipation times are typically seen in impounded (pond) water bodies where there is little outflow of water or a low water exchange (Getsinger, et al, 2000; Petty et al, 1998 and Green et al, 1989). Maximum sediment concentrations typically occur within the first day to one week after application.

Triclopyr residues do not persist in the water column for an extensive period of time. The time of dissipation from the water column to levels below the proposed drinking water residue tolerance (0.5 ppm a.e.) may be as long as 4 weeks in treated ponds but is typically less than 3 weeks in treated ponds (Petty et al, 1998). However, reservoirs and lakes can require up to a 2,000 foot setback distance from potable water intake pipes to avoid human exposure to concentrations higher than the proposed drinking water tolerance of 0.5 ppm a.e. (Ritter and Peacock, 2000 and proposed Garlon® 3A label). The setback distance varies significantly with the size of the treatment area, the concentration of triclopyr being applied and whether submerged or floating/emerged species are the target for control in a potable water source. Problems with livestock exposure are not anticipated since the difference between the potable water tolerance (0.5 ppm a.e.) or the initial application rate (2.5 ppm a.e.) is much lower than the residue tolerance of grass and hay (500 ppm a.e.). Since the residue tolerance on water is so much lower than the residue tolerance on hay, it is expected that a negligible impact on both animal health and meat/milk residues is likely.

Since no studies have been conducted with irrigated crops , the proposed label includes an irrigation use restriction that reads, "Do not use treated water for irrigation for 120 days following application. As an alternative to waiting 120 days, treated water may be used for irrigation once the triclopyr level in the intake water is determined to be non-detectable by laboratory analysis (immunoassay). There is no restriction on the use of *water from treatment areas to irrigate established grasses. For applications to ditches and or/or canals, the label restricts use to non-irrigation situations." Significant metabolism of triclopyr in plants has not been seen on grasses or rice commodities. The only significant residue seen in plant nature of residue studies was triclopyr. No significant levels of the toxic metabolite TCP or other metabolites like TMP have been seen. It is not anticipated that aquatic plants will metabolize triclopyr to any significant degree (EPA RED, 1998). Adsorption of triclopyr is not extensive enough to cause adverse aquatic impact from release of triclopyr after the death of target weed species and nontarget native plant species are often unaffected by use of triclopyr to control submersed aquatic weeds (Netherland and Getsinger, 1993).*

Triclopyr does not adsorb readily to most soil/sediments. The typical range of adsorption coefficients (Kd) on sediments/soils is 0.165 to 0.975 mL/g (Woodburn et al, 1988). In general, a compound with a Kd value of less than 5, and particularly less than 1.0 is considered highly mobile in soil (U.S. EPA, 1986a in Ebasco, 1989). Therefore, under normal conditions, the ability of triclopyr to contaminate ground water appears to be fairly high. However, the limited amount of monitoring prevents the implementation of restricted use criteria. A total of 379 wells from four states have been sampled and only 5 of these wells contain triclopyr residues. These residues range in triclopyr concentration from 0.000006 to 0.00058 ppm a.e. These concentrations are unlikely to cause adverse impact on human subjects since the temporary residue tolerance for drinking water has been set at 0.5 ppm a.e. for triclopyr TEA. However, continued monitoring work may trigger a recommendation of restricted use. More details on the nature of soil mobility and its ecological meaning are discussed in Section 3.

4.2.1.2 Potential for Increased Erosion and Re-suspension of Soils and Sediments from Plant Removal

Summary: Since these Triclopyr TEA products may be applied to wetland associated weeds at concentrations that may remove these weeds, classical erosion effects may occur. However, the main use of these products is to control submerged and floating/emerged weeds. Therefore, depending on the situation, the use of triclopyr TEA may or may not lead to erosion. Also, removal of plants from non-irrigation drainage canal situations may result in erosive processes occurring to a limited extent.

During aquatic weed control, triclopyr TEA products are applied directly to water. Therefore, classic erosion, in a strict sense, generally does not occur from this use. That is, soil and humic material are not dislodged by wind and water and washed into the waterway due to the removal of plants from the adjacent terrestrial environment. Removal of plants from non-flowing water systems may allow for the re-suspension of sediment from the bottom of a lake or pond due to wind mixing of the water, interactions with benthic organisms and direct interfering effects of human beings with the hydrosoil during periods of either work or recreation.

Classical erosion can occur when treatment of wetlands like banks and shores, non-irrigation ditches or canals which have little or no continuous outflow, and areas under forestry or non-cropland conditions occur. Classical erosion may also occur if ponds treated early in the season evaporate or are drawn down. Under such conditions the previously submerged banks and possibly bottom of the lake will temporarily become terrestrial environment subject to classical wind and water erosion. Erosion in these areas would initially be high due to lack of plant cover. However, dead aquatic vegetation or terrestrial vegetation, if not yet broken down by natural decay processes, would function like a mulch to help reduce erosion until the area is re-vegetated with terrestrial plants or the area is flooded or re-flooded with water. A worst case scenario could occur if the area does not re-vegetate before the dead vegetation completely decomposes and exposes the underlying soil/sediment.

Without the presence of plant species providing soil stability, physical characteristics of the soil/sediment are the primary factors affecting soil erosivity. The two most important soil characteristics affecting wind- and water-influence are infiltration capacity and structural stability. Soil texture, organic content, clay content (Brady 1974 in Ebasco, 1993) and structural stability depends on the ability of soil/sediment aggregates to withstand breakup caused by physical bombardment of water and wind. This depends on many factors, including both biological and the organic/inorganic component interaction that provides bridging between organic matter and soil/clays (Brady, 1974 in Ebasco, 1993).

The Soil Conservation Service (USDA, 1978a in Ebasco, 1993) has developed simplified erodibility factors (K) based purely on soil texture of different topsoil and subsoil regimes. These K factors can be used as approximate erosivity estimates. The K values listed in Table 3 are used in predicting rainfall erosion losses with the universal soil loss equation (USDA, 1978b in Ebasco, 1993) and may be used as relative indicators of erosivity across different soil texture classifications.

The loss of soil by wind erosion involves detachment and transport mechanisms. Detachment results from abrasion by both wind and entrained particles. Transport may cause soil particles to travel along the land surface by saltation or to travel parallel to or upward from the land surface by suspension. Soil moisture is the primary factor in determining erosion by wind. Other soil characteristics include mechanical stability of dry soil clods and aggregates, presence of a stable soil crust and bulk density and size of erodible soil fractions (Brady, 1974 in Ebasco, 1993). Once detached, finer-grained particles are most likely to move in the wind and rain. Water erosion has a tendency to have a greater effect on sandy loam than on sediments (particularly silt loam) since water effectively conglomerates and seals the finer soil/sediments. Greater amounts of triclopyr or other pesticides are more likely to wash out of sandy loam than silt loam sediments. Various soil types retained triclopyr at different levels in adsorption experiments. However, since triclopyr is mobile it is likely to be carried into the soil by the action of water and may be less likely to be transported to surface water bodies during runoff, but more likely to be transported into the ground water due to leaching. However, prior to leaching into the soil, triclopyr, due to its high water solubility, may be dissolved and transported to water bodies during runoff.

Re-vegetation of untreated areas can be used to mitigate the problem. It has been recommended that if noxious weed control is necessary in “forest ecosystems” it should be conducted with either herbicides or burning. Mechanical removal of weeds from such an ecosystem increases the rate of erosion. Spot treating problem areas and over-sewing the “forest harvest” area with grasses or herbaceous species that can quickly colonize a site and stabilize soils can further decrease the rate of erosion. Although Neary and Michael (1996) were addressing the problem of harvested forest areas, the approach makes sense for any area where the soil/sediment is not stable.

One is not permitted to use triclopyr TEA to control weeds in canals or ditches that convey large amounts of water. Triclopyr TEA may be used to control weeds in non-irrigation ditches or canals which have little or no continuous flow. However, triclopyr TEA may be used to control weeds growing in non-crop areas which, under a liberal view, could be interpreted as allowing for the control of riparian weeds on the banks and top berms of ditchbanks. In the case of canals treated with triclopyr, erosion is unlikely to be a problem. Generally speaking, the major aquatic weed problems in non-irrigation canals are emergent or riparian weeds growing on the banks of drainage ditches. There are times during the season when these riparian weeds may become a problem. These herbicides are used to control emergent macrophytes. The Garlon® 3A label specifies which emergent and terrestrial species of weeds may be controlled with Triclopyr TEA. However, since efficacy is claimed for above ground species, emergent and riparian weeds like pennywort, purple loosestrife, alligatorweed, plantago, dandelion, Canadian thistle or lambsquarters that are found growing on the banks of drainage ditches and canals are likely to be controlled. Canals typically are constructed with 3:1 bank slopes and are designed to convey peak demand flows without eroding. Drainage canals can be lined with a variety of materials including earth, blended earth (clay mix to reduce seepage loss), asphalt, concrete or geotextile. Although vegetation may invade the channel over time, vegetation-lined channels are typically not constructed because plant growth can reduce the canal’s conveyance capacity. The main objective in canal design is to minimize losses from the canal and to maximize conveyance capacity. Therefore, the irrigation districts actively remove nuisance plant growth from drainage canals. Plant removal operations are usually performed at the end of the irrigation season. The general procedure involves filling and sealing the canal after which the area is treated with a herbicide. The main purpose of triclopyr TEA applications would be to improve drainage water flow by eliminating dense stands of purple loosestrife, alligatorweed or other emergent or riparian weeds. Because drainage canals are typically designed to operate at capacity under un-vegetated conditions, removal of nuisance plants is unlikely to result in destabilization of drainage canals. However, depending on site-specific conditions, erosive processes and the amount of sediment trapped by loosestrife, alligatorweed or other dense stands of weeds, removal of these plants may contribute to limited sediment erosion and transport.

- **Effects of removal of weeds on habitat**

  Removal of weeds from the newly formed or long-standing terrestrial habitat may cause additional silt and nutrients to enter adjacent water bodies. Such an increase in nutrient load may lead to algal blooms and eutrification of the water body. Also, the removal of these terrestrial plants will decrease the amount of terrestrial habitat that terrestrial animals may utilize. Removal of the newly established plants may increase the likelihood of flooding and return the water body to the previous aquatic condition (flooding) or allow for previously un-flooded land to have greater wetland characteristics. Flooding can increase the amount of habitat available for fish and amphibians to utilize for feeding and spawning (Goldman and Horn, 1983). Negative impacts from isolated flooded areas could be stranding or hydrological “jumping” of current flows to a new, but not necessarily superior channel.

4.2.1.3 Effects on Pristine Sites

In general, the prior use of triclopyr does not affect the rate of removal of the pesticide from the aquatic environment. However, long-term use of triclopyr has a small potential to cause adverse impact on mollusc species. However, the only species for which there is good information is the eastern oyster which is possibly susceptible to accidental oversprays of estuarine areas with triclopyr TEA at concentrations seen after treatment with 9 lbs a.e./acre (concentration up to 6.6 ppm a.e. in six inches of water). However, since the LC_{50} of oysters is 22 to 41 ppm a.e., use of triclopyr as a restricted use pesticide is likely to prevent misapplication of triclopyr as described in this paragraph. The fact that oysters and other shellfish are in-faunal organisms may automatically mitigate this problem. It is anticipated that the presence of sediment will decrease the effects of triclopyr on shellfish fisheries by preventing some degree of exposure to the herbicide (Green et al, 1989).

Although it has been reported that bacteria are capable of degrading triclopyr and TCP to carbon dioxide, water and organic acids, working demonstrations of this phenomenon are lacking. However, aerobic and anaerobic soil studies and aquatic studies have shown that these metabolites occur (EPA RED, 1998).

4.2.1.4 Effects on Contaminated Sites

Since triclopyr TEA has only been used experimentally in the field, it is unknown if accumulative impact is likely when triclopyr is used at the same site for a number of years. However, due the high solubility, lack of accumulation on sediment and fairly high rate of degradation (t1/2 = 0.5 to 7.5 days), it seems unlikely that triclopyr will present a high environmental risk due to its yearly use to control aquatic weeds. Even the accumulation of toxic metabolites is unlikely to be a problem since TCP would need to be present in the water column at concentrations of greater than 2.0 ppm a.e. to have adverse impact on humans (EPA RED, 1998). Concentrations of TCP as low as 0.15 may have the potential to adversely impact most sensitive salmonids (LC_{50} = 1.5 ppm for rainbow trout). However, the concentration of TCP rarely exceeds 0.1 ppm and typically completely dissipates in six weeks or less (Petty et al, 1998; Green et al, 1989 and Getsinger et al, 1998). Another potentially fish toxic metabolite (TMP) exhibits concentrations and dissipation curves similar to those displayed by TCP. However, these metabolites are further degraded by bacteria to carbon dioxide, water and organic acids with low toxicity to fish and aquatic invertebrates (EPA, RED, 1998). The ability of bacteria to degrade triclopyr in the environment has been discussed in the previous section. Since sentinel fish (sunfish and catfish) are not significantly affected by treatment with triclopyr at 2.5 ppm a.e., they are probably unaffected by environmental concentrations of TCP or TMP that occur during the normal degradation of triclopyr TEA.

4.2.2 Environmental Persistence

Summary: Although triclopyr does not persist in the water column, it is largely degraded by various species of bacteria. Concentrations of triclopyr accumulated within the plants probably do not degrade but are released intact from dead and dying plants. However, since the plants do not accumulate triclopyr to an extremely high concentration, the release of triclopyr from dead plants is unlikely to adversely impact other healthy plants. Triclopyr can persist in sediment with a half-life of up to 13 days. Triclopyr has been *determined to be quite stable in the absence of light. The hydrolysis half-life for triclopyr acid is longer than 30 days at all normal physiological pHs (pH = 5, 7 and 9). The aerobic aquatic half-life of triclopyr acid is longer than 142 days and the anaerobic aquatic half-life for triclopyr TEA is longer than 2 years. However, triclopyr acid has been determined to be very short-lived on non-flooded soil with a half-life of 8 and 18 days in silty clay loam and silty loam soils, respectively. The main route of degradation for triclopyr acid in the laboratory is aqueous photolysis (half-life 0.6 days). In all cases where microbial degradation occurs the main metabolite appears to be TCP which is further degraded to carbon dioxide and organic acids by various unspecified microbes (EPA RED, 1998, Woodburn and Caranor, 1987 in Getsinger et al, 2000). Peterson et al (1994) estimated that the typical field half-life would be 46 days for triclopyr TEA. However, various authors have found that the field half-life of triclopyr TEA can range from less than one day in Banks Lake, Washington, open water areas of Lake Seminole, Georgia, and riverine areas of the Pend Oreille River, Washington to 3.5 to 7.5 days in protected areas of Lake Seminole, Lake Minnetonka, Minnesota and various ponds in California, Missouri and Texas. Areas where the half-life was short had higher light penetration into the water column and greater water exchange while areas with longer half-lives had light penetration of less than 25 cm and tended to be protected by coves, islands or shoreline land mass on at least three sides of the treatment area. Also, more rapid dissipation was seen when the treatment area was a spot treatment than when a whole water body was treated, particularly if that water body was an impoundment with little or no outflow from the treated area. Triclopyr dissipated to less than 0.01 ppm a.e. in 8 to 14 days in water bodies with half-lives of less than 1 day. Nevertheless, dissipation to concentrations of <0.01 ppm can take 28 to 42 days in water bodies where the half-life is 3.5 to 7.5 days.*

Triclopyr generally does not accumulate in the sediment. The adsorption coefficient is generally less than 1.0 mL/g and therefore, one would not expect the concentration of triclopyr in the sediment to exceed the level of triclopyr in the water column. In field situations, concentrations of triclopyr in the sediment normally do not exceed 0.86 ppm a.e. in areas where very little water exchange occurs. In such areas (ponds), complete dissipation from sediment can take two to four weeks (Petty et al, 1998; Green et al, 1989 and Getsinger et al, 2000). In open waterways, sediment concentrations of triclopyr are somewhat lower (≤0.64 ppm a.e.) with complete dissipation typically occurring in 1 to3 days.

Generally speaking, fish and aquatic invertebrates are unaffected by water or soil contaminated with triclopyr or its TCP and TMP metabolites. Field studies indicate that fish and aquatic invertebrates are not significantly impacted regarding survival when a water body is treated with up to 2.5 ppm a.e. of triclopyr to control aquatic weeds (Houtman et al 1997 and Petty et al, 1998). Even native aquatic plants often survive treatment with triclopyr at concentrations up to 2.5 ppm (Getsinger et al, 1997 and Netherland and Getsinger, 1993) although this high concentration may adversely impact coontail, elodea and southern naiad under impounded water conditions. If triclopyr is classified as a restricted use compound, even the most sensitive estuarine species like eastern oyster are unlikely to be adversely impacted. However, if a safety factor of 10X is included, treatment with triclopyr at 2.5 ppm a.e. may adversely impact the most sensitive estuarine species. However, since direct treatment of estuaries with triclopyr is prohibited, it seems likely that additional dilution before and after treated water enters and estuary should provide an additional safety factor to these most susceptible estuarine organisms.

Bioconcentration occurs at low level in target plants. Eurasian watermilfoil may bioaccumulate triclopyr up to about 10-fold (12 to 19 ppm a.e.) by the third day after treatment at 2.5 ppm a.e. Non target species like flatstem pondweed do not bioaccumulate triclopyr (BCF = 0.53 to 1.41; 1.50 to 3.21 ppm a.e.) and largely eliminate it from their tissue by the 14th day after treatment. The release of triclopyr after the death of target species like Eurasian watermilfoil is not likely to be high enough to have a significant impact on the native aquatic species that survived the initial treatment with triclopyr.

Fish do not bioaccumulate triclopyr or the toxic metabolite TCP in their edible tissue. Field experiments indicate that both game and non-game fish species do not bioaccumulate triclopyr or TCP. The concentrations of triclopyr and TCP are low, and usually do not exceed 0.1 ppm in edible tissue. However, concentrations of triclopyr in crayfish and freshwater clams have been seen at concentrations higher than the temporary shellfish residue tolerance for eight and 21 days, respectively; levels of the toxic metabolite TCP have also been seen at concentrations of up to 0.49 ppm in crayfish for up to 14 days after treatment (Green et al, 1989). Concentrations of triclopyr in inedible fish tissue could be much higher with concentration of triclopyr and TCP in the viscera of bluegills and suckers being ~0.2 ppm and ~ 0.1 ppm a.e., respectively; the concentration of triclopyr and TCP in crayfish viscera were ~0.5 and 0.21 ppm, respectively. Although the concentrations of TMP were higher than TCP, TMP is not considered to be of toxicological significance to humans.

The environmental persistence of triclopyr products in the field can be quite variable; the dissipation half-life in water varies from less than one day to approximately 7.5 days. However, according to most authors, the most typical half-life would be between 3.5 and 7.5 days. Dissipation of triclopyr is primarily due to photolysis, degradation by microbes and mixing of triclopyr treated water with water that has not been treated. After spot treatments of Lake Seminole for the control of Eurasian watermilfoil, triclopyr was not detected at sites located more than 1.5 Km (~5000 feet) downstream. Modeling work indicates that concentrations of triclopyr should not exceed the temporary drinking water tolerance of 0.5 ppm a.e. if the intake pipe is more than 2000 feet from the treatment site even under the most stringent conditions in lakes and reservoirs (Ritter and Peacock, 2000). There is also a 21-day potable water use restriction when triclopyr is applied directly to ponds (impoundment waters).

Triclopyr is not expected to be found on soils as a result of irrigation. Irrigation is prohibited for 120 days after treatment with triclopyr TEA. If a flooding incident occurs within 120 days of application, there is a potential for triclopyr to damage upland sensitive species, particularly grapes, tobacco, vegetable crops and flowers. However, the expected half-life on soils is fairly low (8 to 18 days in the laboratory and two weeks in the field). Therefore, any adverse impact due to a flooding incident is likely to be quite limited.

4.2.2.1 In Water

A detailed review of the persistence of triclopyr in water can be found in Section 3.1.3.3. The dissipation half-life for triclopyr ranges from less than 1 day to 7.5 days (Getsinger et al, 1977 in Getsinger et al, 2000; Green et al, 1989; Getsinger et al 2000; Getsinger et al, 1997; Petty et al, 1998 and Houtman et al, 1997) (Table 5).

Shorter half-lives appear to be correlated with transmittance of light to deeper depths, and open, slow flowing or riverine areas. Both the extent of vegetative cover and the type of vegetation can influence light transmittance. Sites with rapid dissipation of triclopyr included riverine areas of the Pend Oreille River, shallow areas open on at least three sides in Lake Seminole, Georgia, and areas experiencing high winds (10 to 15 mph gusting to 20 mph) in Banks Lake, Washington. Concentrations of triclopyr in these sites with short half-lives will typically fall below the temporary drinking water tolerance within 3 days of application. In areas with short triclopyr half-lives, the metabolite TCP is often not detected after the day of treatment, but has been detected at concentrations of 0.05 to 0.14 ppm in Lake Seminole.

Longer half-lives appear to be correlated with reduced light transmittance, deeper depths, areas of treatment located in coves or protected by land masses on at least three sides, and impounded water with little or no out-flow from the treated area. Sites with slow degradation have been found in embayments (coves) of Lake Minnetonka (t1/2 = 3.7 to 4.7 days), deep water areas protected by land masses in Lake Seminole (t1/2 = 3.5 days) coves of the Pend Orielle River, and ponds located in Elk Grove, California (t1/2 = 6.9 to 7.5 days), Columbia, Missouri (t1/2 = 5.9 to 6.1 days) and Lewisville, Texas (t1/2 = 6.3 to 6.5 days). In the Missouri pond where the greatest light transmittance occurred, the half-life of triclopyr was the shortest. However, the authors noted that photolysis may play a minimal role in the degradation of triclopyr in pond and other surface water situations (Petty et al, 1998). Since the rate of degradation does not seem to vary by more than two-fold even when light transmittance is extensive, it appears that the degradation of triclopyr by bacteria and other microbes to TCP, TMP and further to carbon dioxide, water and organic acids is likely to be the main route of degradation. Further dissipation of triclopyr in the water column can occur due to mixing with water from untreated areas in rivers, and large lakes where spot treatments are used to control aquatic weeds. At any rate, triclopyr and its toxic metabolite TCP degrade and dissipate rapidly through chemical, biological and physical processes (Various authors in Houtman et al, 1997). The concentrations of triclopyr in lakes that have been spot treated generally fall below the temporary drinking water residue tolerance (0.5 ppm a.e.) within three to eight days of application. However, the concentration of triclopyr in ponds can take three to four weeks to dissipate to concentrations below 0.5 ppm a.e. Furthermore, the concentration of the toxic metabolite (TCP) has generally been low in lake and pond water with concentrations of TCP not higher than ~0.1 ppm in Lake Minnetonka, Lake Seminole, various ponds on the day of application and generally dissipating to concentrations below the detection limit at 3 days after treatment. Although bacterial (biotic) metabolism has been cited as main mechanism for the degradation of both triclopyr and it toxic metabolite TCP, the species of bacteria were not specified. It is possible that the same species that typically degrade 2,4-D may also be responsible for the degradation of triclopyr. These species may include *Acaligenes eutrophus, Arthrobacter, Bordetella, Flavobacterium, Pseudomonas* and *Xanthobacter*. It would be interesting to conduct experiments with the bacteria that are known to degrade 2,4-D to discover if these species of bacteria are also capable of metabolizing triclopyr TEA to the aforementioned metabolites and whether or not these species are capable of using triclopyr as a sole carbon energy source. See Section 4.2.1.3 in the 2,4-D SEIS Appendix C (2000).

4.2.2.2 In Sediment

A detailed review of the persistence of triclopyr in sediment can be found in Section 3.1.3.2. Triclopyr from the application of Garlon® 3A or Renovate® may have long half-lives in sediment. In deep sediments under anaerobic condition, triclopyr degrades to TCP with a half-life of about 3.5 years (Ladowski and Didlack (1984 in Petty et al, 1998). However, in more typical situations where water is fairly shallow (0.3 to less than two meters), the stability of triclopyr in sediment is very much reduced with half-lives that range from less than one day at Lake Seminole to 5.8 days in Lake Minnetonka. Since the distribution coefficient for triclopyr is low (0.165 to 0.925 mL/g), it is not anticipated that it would bind tightly to sediment and therefore concentration in sediment should remain low. This assumption is confirmed by results from field studies. For example, at Lake Minnetonka, concentrations of triclopyr in sediment were never higher than 0.334 ppm a.e. and dissipation to concentrations of $\leq$0.15 ppm were seen within 14 days after application. At Lake Seminole, triclopyr was not seen at significant concentrations (<0.1 ppm a.e.) except for the day of application where concentrations as high as 0.64 ppm a.e. were detected. Even in the pond studies the concentration of triclopyr in sediment was very low and did not exceed 0.86 ppm a.e. during the first few days and dissipated to below the limit of quantitation within 4 weeks. These low levels of triclopyr in sediment indicate that the sediment quality should remain high in treated water bodies and that such sediments should pose little or no threat to benthic in-fauna. The toxic metabolite TCP is found at even lower concentrations than triclopyr. Both laboratory and field studies indicate the concentrations of TCP in the sediment are very low and generally do not exceed 0.16 ppm and are typically less than 0.05 ppm in lakes and ponds. TCP generally dissipates to below the level of quantitation within a few days of application to lakes but may take up to six weeks to entirely dissipate from ponds. Another metabolite (TMP) is rarely detected in lake or pond sediment and is normally detected in the water column at concentrations that do not exceed 0.01 ppm a.e. TMP is generally considered to have no toxicological significance. Data supporting these conclusions can be found in Getsinger et al, (2000) Petty et al (1998) and Green et al (1989) (Table 5).

4.2.2.3 In Soil

The presence of triclopyr in soil is not anticipated from aquatic treatment unless flooding occurs or the water is used for irrigation. The proposed label prohibits use of triclopyr treated water for irrigation for 120 days after application (proposed Garlon® 3A label, 2000). The length of this water use restriction may be shortened if triclopyr is not detected in water taken from treated water bodies. However, triclopyr may be found in wetland soils after treatment of non-flooded non-crop areas with up to 9 lbs a.e./acre. Immediately after application, triclopyr is expected at concentrations up to 6.6 ppm a.e. in bare soil samples 15 cm in depth. However, high residues are not anticipated to remain on treated soil since the half-life of triclopyr on soil is typically ~11 days. Generally speaking, applications of triclopyr at 8.1 lbs a.e./acre had concentrations of triclopyr of 0.14 ppm a.e. in the 15 to 30-cm soil segment after 4-weeks of aging and 0.02 ppm at all later sampling intervals. Significant concentrations of triclopyr may be found on soils associated with turf-grasses and pasture land since there is no restriction on the irrigation of these turf and pastureland sites with water that has been treated with triclopyr TEA (Garlon® 3A label). This is not considered to be a potential problem with livestock since the residue tolerance on pastureland grasses is 500 ppm a.e. The metabolites (TCP and TMP) may be found on soils treated with triclopyr at concentrations of 6.4 to 8 lbs a.e./acre. These two degradates can be found in soil at rates up to 0.18 and 0.35 ppm, respectively. However, less than 0.10 ppm of TCP and TMP are found in soils after 8 weeks of aging (EPA RED, 1998).

4.2.2.4 Potential for Bioaccumulation or Bioconcentration in Fish, Aquatic Invertebrates, Phytoplankton, Zooplankton, Birds, Mammals and Insects

Summary: Bioaccumulation generally does not occur at even moderately high levels in any aquatic organisms except target plants like Eurasian watermilfoil where a BCF (Bioconcentration Factor) value of ~10-fold may occur. BCF levels in non-target plants, fish, and shellfish typically do not exceed ~2-fold. In edible fish tissue, the concentration of triclopyr does not exceed the temporary fish residue tolerance of 0.2 ppm a.e. Therefore, fishing restrictions are not necessary after application of triclopyr TEA. Freshwater clams and crayfish may accumulate residues as high as 2.49 and 4.87 ppm a.e., respectively. Furthermore, it can take from 8 to 21 days, respectively for clams and crayfish to dissipate triclopyr to levels below the temporary shellfish residue tolerance. Therefore, a shellfish harvest restriction of up to 21 days may be necessary. Triclopyr does not generally accumulate in eggs and milk or in animal tissue at concentrations that exceed 0.1 ppm a.e. Typically livestock animals eliminate more than 90% of the total triclopyr residue and metabolites in their excreta (chickens) or in their urine (goats).

- **Bioaccumulation and bioconcentration**

The potential for bioaccumulation (BAF) and bioconcentration (BCF) is low to moderate for triclopyr. In some cases triclopyr will be adsorbed at concentrations of up to 19 ppm (BCF =10) on Eurasian watermilfoil. Target species of plants appear to continue to adsorb triclopyr until mortality occurs. However, nontarget plants like broadleaf pondweed, do not adsorb triclopyr to any appreciable level (<3.2 ppm a.e.; BCF = 1.4), and within 14 days the nontarget plants have dissipated triclopyr to less than 0.21 ppm a.e. (Getsinger et al, 2000). Mixed stands of Eurasian watermilfoil and *Hydrilla verticillata* have been observed to adsorb triclopyr at concentrations up to 5.66 ppm a.e. on the day of application (Lake Seminole), but triclopyr was not detected at concentrations higher than 0.003 ppm a.e. eight days after application. It has been postulated that non-target plants like coontail, naiad, elodea and flatstem pondweed may avoid the toxic effects of triclopyr by not absorpting this herbicide. Although no work has been done on the metabolism of triclopyr in aquatic plants, it has been observed on terrestrial grasses and rice commodities that triclopyr is not metabolized (EPA RED, 1998).

The bioconcentration factor can be predicted throughout most of its range from the following equation: BCF = K_{ow} x 0.05. Since the octanol/water partition coefficient is very low (K_{ow} = 0.169 to 4.24) for all reasonable pHs (pH 5 to 9), EPA has not required that bioconcentration studies be conducted with fish or shellfish. The predicted BCF would be less than 0.2 based on the K_{ow}.

However, laboratory tests with bluegill sunfish found that triclopyr and its metabolites did not bioaccumulate when fish were exposed to 2.5 ppm triclopyr TEA for 96 hours. The highest 14C-total residue concentration was found to be 0.13 ppm in edible tissue, 2.33 ppm in inedible tissue and 1.39 ppm in whole fish. At all time periods the bioconcentration factor was less than 0.05 in edible tissue, 0.93 in inedible tissue and 0.56 in whole fish. After 96 hours of exposure the edible tissue contained 0.029 ppm triclopyr, 0.009 TMP and 0.06 ppm. After 72 hours of depuration, 80% of the radiolabeled residues depurated from edible tissue(Lickly and Murphy, 1987).

In field studies, where ponds were treated with 2.5 ppm a.e. triclopyr TEA, the concentrations (<0.03 ppm a.e.) of triclopyr found in edible bluegill sunfish tissue was always below the temporary fish residue tolerance of 0.2 ppm a.e. (Table 5, Petty et al, 1997). Similar work in the same ponds and in Lake Minnetonka and Lake Seminole found similar results with edible tissue in a variety of fish including largemouth bass, bluegill sunfish, suckers, common carp, chain pickerel, gizzard shad, Lake chubsucker, spotted sucker, redear sunfish, warmouth sunfish and yellow perch (Getsinger et al, 2000 and Green et al, 1989). The toxic metabolite TCP was not normally detected in edible fish tissue. However, TCP was detected at concentrations as high as 0.07 ppm in bluegill sunfish. The concentrations of TCP in edible fish tissue were normally <0.03 ppm. The concentration of the more lipophilic TMP is generally somewhat higher than triclopyr or TCP in edible fish tissue. However, TMP is not of toxicological concern to mammals and is generally ignored in the residue tolerance expression. In non-edible tissue (viscera, heads and skin) the concentrations of triclopyr are often seen to be somewhat higher than the residue tolerance for triclopyr. Concentrations of triclopyr, TCP and TMP have been recorded as high 0.3, 0.2 and 0.8, respectively in non-edible fish tissue during the first few days after treatment, but generally dissipate to concentrations below 0.2 ppm within a couple of weeks. The exception to this is the less polar TMP metabolite which may be retained for longer periods of time.

Concentrations of triclopyr and its toxic metabolite TCP have been observed at higher levels in crayfish and freshwater clams. Concentrations of triclopyr in crayfish have been detected at Lake Seminole as high as 4.87 ppm a.e. on the day of application. It may take as long as or longer than 21 days for triclopyr to depurate to levels below the temporary crayfish residue tolerance of 0.2 ppm. Concentrations of TCP in crayfish can rise as high as 0.49 ppm four days after treatment but drop to below 0.05 ppm by 21 days after treatment. Similar observations have been made with freshwater clams. However, depuration from the high concentration of 2.49 ppm a.e. to <0.2 ppm usually only takes 8 days and TCP concentrations are generally not detected at concentrations higher than 0.06 ppm and then only during the first few days after exposure. However, laboratory work with crayfish exposed to 2.5 ppm a.e. had concentrations of triclopyr in tail muscle and hepatopancreas that were not higher than 0.3 and 1.3 ppm a.e., respectively. Hepatopancreas extracts contained more than 80% triclopyr and about 10% of the triclopyr-taurine conjugate. After 36 days of depuration ~80% of the total residue had depurated from the tail muscle and hepatopancreas (Barron et al, 1991).

Mammals and birds do not bioaccumulate triclopyr. In mammals and birds fed ^{14}C-labeled triclopyr, ~98 % of the applied radiation is excreted. In mammals (goats) more than 88% of the applied radiation is excreted in the urine and in birds (chickens) 98% of the applied radiation is excreted in the bird excreta. At concentrations that mimic exposure to real life levels of triclopyr levels in milk, egg and tissue are typically less than 0.1 ppm a.e. The main metabolite is TCP and other metabolites include conjugates of TCP and triclopyr.

- **Persistence within the organism**

Most organisms do not bioconcentrate triclopyr and those that do rapidly eliminate the compound. Fish that adsorbed triclopyr from the water eliminated the majority (more than 80%) of triclopyr from their edible tissues within a few days (Lickly and Murphy, 1987; Barron et al, 1991; Green et al, 1989, Petty et al, 1998 and Getsinger, 2000). However, triclopyr and its metabolites (TCP and TMP) may be retained in the vicera of fish and shellfish for several weeks.

Over 20% (0.029 ppm a.e.) of the triclopyr detectable in edible muscle tissue of bluegill sunfish remained as unchanged triclopyr after 4 days of exposure to 14C-labled triclopyr TEA (Lickly and Murphy, 1987). Other metabolites that were detected included 7% (0.009 ppm) of TCP, 14% TMP (0.0018 ppm) and 46% unidentified organic extractable metabolites (0.06 ppm). Furthermore, in field tests where ponds were treated with 2.5 ppm a.e. triclopyr TEA, the main residue in edible tissue varied depending on how long after treatment the edible tissue was evaluated (Petty et al, 1997). On the first day of treatment, the main residues were triclopyr and TMP; after several days the main residues were TCP and TMP. TMP was usually the detectable residue in highest concentration and had a tendency to remain in edible tissues for a number of weeks longer than the other residues. Fortunately TMP is not considered to be toxicologically significant to mammals including humans.

Over 80% of the 14C-label triclopyr detected in crayfish tail muscle and hepatopancreas was dissipated in 36 days. However, while the total residues in tail muscle did not exceed 0.052 ppm a.e. after dissipation, total residue concentrations in the hepatopancreas were 0.337 ppm a.e. even after 36 days of dissipation. The hepatopancreas is eaten in some areas of the United States (Deep South), in most areas it is considered inedible. Therefore, a concentration of triclopyr in the hepatopancreas that exceed the shellfish residue tolerance (0.2 ppm a.e.) is generally not an issue.

In domestic animals, the administered dose was 3-grams/goat/ day for 10 days or 1.1-grams/hen/day for 10 days. Very large amounts of the dosage are eliminated in the urine (>88%) of goats and in the excreta of hens (99.7%). Generally speaking, <0.1 ppm of total residue was detected in eggs, milk or tissue of chickens and/or goats. However, the level of total residues detected in kidney and liver of goats was 0.3 to 0.4 ppm. In chickens, the only residue of significance that was found in tissues (kidney liver and skin with 0.7, 0.09 and 0.07 ppm total residue respectively) with enough total residue to analyze was triclopyr and a conjugate of triclopyr (0.02%). In goats, the levels of triclopyr in tissue and milk was typically around 20% to 30% of the total tissue residue except for liver where the percentage of triclopyr in the tissue was only 0.2%. Most of the remaining residues in goat tissues were TCP. Absolute tissue residence time for these residues could not be determined since the animals were sacrificed 24 hours after the last dosage and these studies are not designed to be toxicokinetic studies (Puvanesarajah, 1992; Hamburg et al 1987; Bauriedel, 1983 and Yankovich and Bauriedel, 1976).

- **Potential impacts on the food chain**

  Triclopyr has a slight tendency to accumulate (up to 10 fold) in target plants. Triclopyr does not accumulate in sediment, nontarget plants, fish, shellfish, mammals or birds. Since the bioaccumulation factor in all cases is ≤10-fold, triclopyr is non-accumulative according to the work of Weber (1977 as cited in EBASCO, 1993) (Table 5). In most cases, triclopyr does not persist in sediment, plants or animals for long periods of time. However, triclopyr has been observed to persist for up to 3.5 years in anaerobic sediment underlying deep water (Ladowski and Didlack, 1984 in Petty, 1998). In most cases, triclopyr has dissipated from sediment within one month of treatment (Table 5) and its main metabolite (TCP) is also not detected at significant concentrations. Concentrations of triclopyr in target plant species continue to accumulate until the plants die, which may take from 3 days to several weeks (Getsinger et al 2000 and Netherland and Getsinger, 1993).

  Since the concentrations of triclopyr in plants has not been reported higher than 19 ppm after treatment and the water volume is great compared to the plant volume, the release of triclopyr after plant death is not anticipated to cause further impact on aquatic plants or animals. Bacteria and other microbes in the water column and sediment metabolize triclopyr and its metabolites to carbon dioxide, water and various organic acids. However, mixing with untreated water in open waterways and photolysis also influences the dissipation of triclopyr and its metabolites by sunlight in shallow waterways with limited plant cover.

  Animals (terrestrial vertebrates), while adsorbing triclopyr from their intestinal tract, rapidly eliminate it in the urine (mammals) and excreta (chickens) primarily as unchanged triclopyr. Triclopyr and its metabolites are not typically detected in eggs, milk and tissues at concentrations higher than 0.1 ppm total residue. However, the concentrations of total residue in kidneys and liver can be as high as 0.3 to 0.4 ppm in goats and up to 0.7 ppm in chickens. Triclopyr residues are ~20 to 30% in goats and 85% in chickens and the main metabolite is TCP.

  In the only fish species tested, the concentration of triclopyr in edible tissue is not higher than 0.029 ppm after 96 hours of exposure with TCP and TMP concentrations occurring at 0.009 ppm and 0.018 ppm, respectively. Approximately 50% of triclopyr dissipates from edible fish tissue in 72 hours and ~66% and ~80% of the TCP and TMP dissipates from edible fish tissue in 72 hours (Lickly and Murphy, 1987). Field concentrations of triclopyr and its TCP metabolite have been shown to remain low (Table 5). Triclopyr and TCP are typically detected at concentrations considerably lower than 0.1 ppm in the edible tissue of a variety of game and non-game fish. Triclopyr and TCP have also been observed to remain low in the viscera of game and non-game fish with concentration rarely exceeding 0.3 ppm. Since the concentrations of triclopyr and its toxic metabolite (TCP) remain below the temporary residue tolerance in edible tissue, spot treatments in lakes and whole pond treatments should not affect fisheries, fishing or the consumption of fish by humans. Furthermore, since game fish do not appear to accumulate triclopyr or TCP at concentrations that are any higher than forage fish, it appears unlikely that triclopyr or TCP will be biomagnified as it travels up trophic levels (Green et al, 1989).

Although laboratory work indicates that crayfish bioaccumulate triclopyr and its metabolite (triclopyr-taurine conjugate) at the same rate as fish, field studies show that accumulation of triclopyr and its metabolite in shellfish may be significantly higher than in fish (Barron et al, 1991 and Green et al, 1989). However, the rate of depuration of the total residues may be much slower than is typically seen in fish. For example: In the field, shellfish may bioaccumulate triclopyr at concentrations that are higher than the temporary shellfish tolerance of 0.2 ppm. Crayfish taken from Lake Seminole waters treated with 2.5 ppm a.e. triclopyr TEA, had concentrations that ranged from 0.76 to 4.87 ppm a.e. for the first 14 days after treatment. It may take 21 or more days after treatment for the concentrations of triclopyr to fall below the temporary residue tolerance. The metabolite TCP has been detected at 0.49 ppm 14 days after treatment with triclopyr, but was not seen at significant concentrations 21 days after treatment. Similar results were observed with fresh water clams. However, concentrations of 2.49 ppm a.e. in freshwater clams took up to 8 days to dissipate below the temporary residue tolerance of 0.2 ppm a.e. while TCP was not detected at concentrations higher than 0.06 ppm. The high concentrations of triclopyr seen in crayfish may have been an artifact since crayfish were housed in cages and did not have contact with the sediment. Green et al (1989) indicated that concentrations in crayfish tissue would probably have been lower if the crayfish had been able to burrow into the sediment as is typical for this in-faunal organism. Further work is necessary to determine concentrations of triclopyr, and its metabolites found in shellfish warrant a restriction on taking crayfish and bivalves when the label for Garlon® 3A and Renovate® are released. The current experimental label for Renovate® specifies a 2-week shellfish harvest restriction and a 30-day fishing restriction after treatment with Renovate® has occurred.

Therefore, triclopyr should not bioaccumulate and should be rapidly eliminated from most organisms that ingest it. Triclopyr should also not be bioaccumulated (biomagnified) as it is passed up the food chain.

4.2.3 Potential Impacts of Water Quality on Survival of Aquatic Organisms

4.2.3.1 Effects of Physiological Sustaining Water Chemistry

Summary: Exposure of living plant tissue to triclopyr products or other herbicides usually results in secondary effects that may impact the biota. When plants start to die, there is often a drop in the dissolved oxygen content associated with the decay of the dead and dying plant material. Reduction in dissolved oxygen concentration may result in aquatic animal mortality or a shift in dominant forms to those more tolerant of anaerobic conditions. There may also be changes in the levels of plant nutrients due to release of phosphate from the decaying plant tissue and the anoxic hypolimnion. Ammonia may also be produced from the decay of dead and dying plant tissue, which may reach levels toxic to the resident biota. Ammonia may be further oxidized to nitrite (which is also toxic to fish), and the almost nontoxic, nitrate. The presence of these nutrients may cause an algal bloom to occur. However, if significant living plant biomass persists after treatment, the released nutrients may be removed before an algal bloom can occur. Hardness, pH, turbidity, dissolved oxygen content and conductivity influence water quality. Although water quality changed as a result of diel effects and seasonal changes have been seen, water quality changes associated with triclopyr use have not been observed in treated lakes and ponds. In both treated and untreated ponds, DO (Dissolved Oxygen) concentrations were usually high during the daytime (~10 ppm or higher) and approximately zero at nighttime. These high levels of DO during the daylight hours are due to high levels of algae in these ponds. The low DO levels are due respiratory effects from large amounts of algae and macrophytes that do not produce *oxygen by photosynthesis during the nighttime. In some cases, the removal of Eurasian watermilfoil by treatment with triclopyr allowed the DO content to rebound until native plant populations resurged and DO levels dropped again. In the presence of large amounts of aquatic vegetation, DO is typically suppressed by restricted water circulation and oxygen consumption by plant respiration near the bottom of the water body where photosynthesis is reduced. Gradual increases in daily pH maximum during the season were observed in both treated and untreated lakes and ponds. The maximum daily pH increased from ~7.5 at the beginning of the season to ~10.0 later in the season. This increase is due to the removal of carbon dioxide from the ponds as a result of photosynthesis. Conductivity, which is a reflection of water hardness, also had a tendency to increase in the early part of the season. Total dissolved solids, light penetration and secchi disc transparency, when it was measured, generally remained at about the same levels in both treated and untreated ponds. Experiments on the effects of pH on the toxicity of triclopyr TEA were not conducted. Since the pKa of triclopyr acid is 2.68, it is unlikely that normal physiological pHs will affect the toxicity of triclopyr. At extremely acid pHs, the toxicity of triclopyr may be increased since greater proportions of triclopyr will exist in the acid form and less triclopyr will exist as the conjugate base form.*

- **Potential impacts of dissolved oxygen**

  The key factor to survival and maintenance of most organisms in the aquatic environment is adequate dissolved oxygen. The oxygen content of the water should ideally be as close to saturation as possible. For warm water environments (15 to 25°C), oxygen saturation is 10 mg/L at 15°C and 8.2 mg/L at 25°C. For cold water environments (5° to 15°C), oxygen saturation is 12.2 mg/L at 5°C and 10 mg/L at 15°C. Cold and warm waters are somewhat arbitrary designations. Table 6 shows the sea level saturation concentration for oxygen at temperatures from 5° to 25°C.

  Warm water fish like sunfish, bass, catfish, carp and shiners can generally survive and reproduce at oxygen concentrations of about 5 mg/L (Litler, 1983, personal communications). While cold water fish are able to survive for short periods at dissolved oxygen concentrations as low as 1 to 3 mg/L, concentrations needed for long term survival are much higher. It is unlikely that these cold water species could go through a life-cycle at dissolved oxygen concentrations below 9.0 mg/L (Welch, 1992 in Shearer et al, 1996).

  Treatment with triclopyr products has not been shown to decrease dissolved oxygen content. Oxygen depletions are to be expected following application of triclopyr due to the bacterial breakdown of dead plants. Even though triclopyr treatments have been shown to cause the death and subsequent decay of target plants, dissolved oxygen content was not believed to have been affected by this decay. The dissolved oxygen content remained the same in both treated and untreated sites at Lake Seminole, Lake Minnetonka, and ponds in California, Missouri and Texas (Petty et al, 1998, Houtman et al, 1998, Green et al, 1989). However, low oxygen concentrations have caused significant fish mortality in ponds treated with triclopyr TEA at concentrations of 2.5 ppm a.e. For example, 26% of the suckers, 11% of the largemouth bass and 5% of the bluegill died at Lake Minnetonka sites where triclopyr was used for control of Eurasian watermilfoil. However, similar or higher rates of mortality were seen in plots that had not been treated with triclopyr TEA. The mortalities observed were believed to be due to an observed oxygen sag. However, this oxygen sag did not impact brown bullhead, crayfish or clams in either the control of treatment sites (Houtman et al, 1997). Similar work in a pond in Texas (Houtman et al, 1998) found that sunfish had a mortality of less than 1% and catfish suffered 10% mortality in treated ponds and only 3% in the control ponds. The fish mortality levels in both treated and control ponds are acceptable and not significantly different.

Although triclopyr generally dissipates rapidly in water and sediment, it is known that anaerobic conditions can affect the rate of triclopyr degradation. For example, triclopyr has been observed in the field to have a half-life of 3.5 years in anaerobic sediment located at the bottom of a deep water column (Ladowski and Didlack, 1984 in Petty, 1998). This data indicates that the degradation rate of triclopyr may be affected by the presence of well oxygenated sediment. However, the main routes of dissipation in the field may be due to dilution with untreated water, and photolysis in shallow water with low plant cover. These results gain considerable credibility since laboratory aquatic studies under both anaerobic and aerobic conditions have shown that triclopyr acid persists for 365 and >142 days, respectively with only 80% and 50% degradation, respectively (EPA RED, 1998).

- **Potential impacts of ammonia, nitrite and nitrate production**

It is rare when nitrogen is the limiting factor for production within a freshwater body. Several species of blue-green algae have the ability to fix nitrogen. Therefore, additions of nitrogen to water bodies is not a major issue. However, the toxicity of ammonia and nitrites to aquatic organisms can be important. Nevertheless, measurements of ammonia, nitrate and nitrite levels were not part of the water quality measurements after treatment with triclopyr TEA in Lake Minnetonka, Lake Seminole and ponds in California, Missouri and Texas. Although algal blooms dominated by green algae and diatom species were observed in ponds treated with 2.5 ppm a.e. triclopyr TEA, healthy and diverse populations of algae were seen in both treated and untreated ponds. Blue-green algae were seen to decrease to a greater degree in some of the treatment sites than in the control sites. However, the dominance of green algae species in all ponds may have been due to moderate and stable spring and summer maximum water temperatures (25°-30°C) rather than the direct effects of triclopyr TEA or the release of nutrient nitrates, nitrites or ammonia. Genera of green algae that seem to thrive at these temperatures included *Spirogyra, Mougeotia, Volvox, Closterium* and *Scenedesmus*.

In Washington waters, even a small release of ammonia can be a serious issue. The whole lake levels of ammonia-nitrogen in Lake Steilacoom during the 1995 season exceeded the aquatic life criteria of 0.100 mg/L during the months of May and October. These levels of ammonia are toxic to fish and near-shore runoff containing fertilizers may have contributed to the October ammonia peak (Shearer et al, 1996). These levels of ammonia are higher than the maximum recommended levels for the culture of aquatic organisms and are higher than the EPA criterion (0.091 mg/L) for 4-day exposure of salmonids.

The toxicity of ammonia increases with both temperature and pH. As temperature and pH increase, the amount of unionized ammonia increases (Table 7). The unionized forms of ammonia (NH4OH + NH3) are toxic to aquatic animals. The ionized form of ammonia ($NH4^+$) is almost harmless (Goldman and Horne, 1983).

Adsorption of nitrogen containing nutrients by aquatic macrophytes and algae can influence the seasonal dynamics of nitrite and nitrate concentrations. The levels of nitrite/nitrate are often higher at the surface of a non-flowing water body than at the bottom because under anoxic conditions some bacteria utilize nitrate as a terminal hydrogen receptor when oxygen is not available.

Nitrite, although fairly toxic, is rarely a problem in well aerated waters because it is rapidly converted to nitrate and under anoxic conditions it is rapidly converted to ammonia. Nitrate is usually not toxic in the quantities found in lakes and rivers (up to 1 ppm). The drinking water standard is set at about 10 ppm. Polluted streams can contain up to 2 ppm of nitrite and small areas near the thermocline may contain relatively large quantities of nitrite.

If nitrogen is the limiting nutrient, nitrate can participate in the next algal bloom. Nitrate and nitrite are formed from the oxidation of ammonia and may persist long after algae and plants have utilized the ammonia in their biological processes. The next algal bloom can be due to the presence of nitrate. However, it may take several days from the time ammonia becomes in short supply for the next bloom to occur because nitrate uptake is slow relative to ammonia uptake and induction of nitrate reductase in algae is also fairly slow. Nitrate must be reduced to ammonia in algae prior to the initiation of an algal bloom (Goldman and Horne, 1983).

- **Potential impacts of nutrient cycling and the release of phosphates and other plant nutrients**

  Phosphate is usually the limiting nutrient in aquatic systems because it is tied up in growing plant and animal tissue as well as the sediment. The sediment typically retains phosphorus under aerobic conditions and releases it under anaerobic conditions. This released phosphate may result in growth of phytoplankton in the hypolimnion provided the depth is not so great that photosynthesis is precluded. When plants are treated with triclopyr or other herbicides they die, and degradation of plant tissue by microbes can cause phosphate and other nutrients to be released. However, the levels of phosphorous were not monitored as part of the water quality studies at Lake Minnetonka, Lake Seminole or ponds in California, Missouri and Texas. Although alga blooms dominated by green algal and diatom species were observed in ponds treated with 2.5 ppm a.e. triclopyr TEA, healthy and diverse populations of algae were seen in both treated and untreated ponds. Blue-green algae were seen to decrease to a greater degree in some of the treatment sites than in the control sites. However, the dominance of green algae species in all ponds may have been due to moderate and stable spring and summer maximum water temperatures (25°-30°C) rather than the direct effects of triclopyr TEA or the release of nutrient orthophosphates. Genera of green algae that seem to thrive at these temperatures include *Spirogyra, Mougeotia, Volvox, Closterium* and *Scenedesmus.*

  Phosphorous in its organic form, cannot be utilized and must first be converted to phosphate (PO_4) by excretion and decay. Normally, phosphates will be at very low levels and rarely exceed 0.020 mg/L in the summer or 0.030 mg/L in the winter. Nitrate and ammonia levels are often many times higher than phosphate levels, and plants typically require a 7:1 nitrogen/phosphate ratio by weight for maximum growth rate. However, phosphorous depletion is likely in freshwaters under normal circumstances. Therefore, the treatment of a water body with triclopyr, which causes release of phosphates from the decaying tissue after the plants have died, has the potential to cause an algal bloom.

The only other nutrient, frequently in short supply, is iron. Ferric iron may either react with or be adsorbed with phosphate into the sediments under typical aerobic conditions and become biologically unavailable. Under anaerobic conditions, ferrous iron is formed from ferric iron/phosphate complexes and is released into the hypolimnion where plants may utilize it for growth, provided that the light is sufficient for photosynthesis to occur. Eh (oxidation/reduction potential), pH and DOC (dissolved oxygen content) govern this reaction. The heterogeneous nature of water/sediment phase reactions prevents easy extrapolation of laboratory results to real lake and pond sediment systems. Iron availability may limit the growth of algae in lakes and streams especially when the production of ammonia (due to nitrogen fixation) is the limiting factor in algal growth (Goldman & Horne, 1983 and Reid, 1961).

Nutrient cycling typically starts with a bloom of algae, and ends when one of the nutrients and/or other factors becomes in short supply. At that point the algae die and release phosphates, iron and ammonia through the degradative process. When enough of the nutrient in shortest supply becomes sufficient to sustain growth, algae will start growing again in the lag phase and will result in an algal bloom if conditions of temperature, pH, N: P ratio and iron concentration are adequate to sustain a log phase growth.

- **Potential impacts of pH changes**

The pH of most natural waters falls between 4 and 9. A pH of 7 is neutral, neither acid nor basic. One way in which pH is controlled is by removing carbon-dioxide from the water. A pH of greater than 8 in a lake or pond is probably due largely to a high rate of photosynthesis, which increases pH by removing carbon dioxide from the water. Anthropogenic sources of high pH include enrichment of the water with fertilizers containing organophosphates. If the pH of a lake or pond is low (<6) it is likely due to leaching of organic acids from peat, and anthropogenic sources such as acid rain or leachate from mines. Bottom waters are typically lower in pH than surface waters because bacterial respiration and decomposition of organic matter produces carbon dioxide and organic acids which lower pH (Shearer, 1996).

After aquatic macrophytes die, due to either natural process or treatment with an herbicide, the pH may drop. If an algal bloom occurs after the release of nutrients, the pH may rise due to the removal of carbon dioxide from the water column by photosynthesis. A pH greater than 9 can be directly lethal to fish. Toxicity to high pH levels arises from the inhibition of ammonia secretion by gills and respiratory alkalosis (Heath, 1995 in Shearer, 1996). Sub-lethal alkaline or acidic conditions can indirectly harm fish and other aquatic animals by increasing their susceptibility to other stresses such a pollutants (like triclopyr), ammonia, high temperatures and low dissolved oxygen. The pH levels were observed to exhibit a diel pattern in Lake Minnetonka, Lake Seminole and the ponds in California, Missouri and Texas. The pH was generally low at night (pH = ~7.5) and higher during daylight hours (pH =

~9.0 to ~10). These pH changes were observed in both treatment and non-treatment plots. While these pH changes were often correlated with algal blooms, the algal blooms were similar in both treated and untreated plots.

The effects of hardness and pH have not been studied with triclopyr and since the dissociation constant (pKa) is 2.68, it seems unlikely that changes in hardness and pH typically found in biologically viable water bodies, would affect the toxicity of triclopyr. For pH to have an affect on triclopyr toxicity, it would probably be necessary for the pH to be less than 3.0 where a significant amount of the triclopyr would be in the acid form rather than its conjugate base form.

4.2.3.2 Effects of Triclopyr in Water

Summary: In the State of Washington, pesticide residues that exceed the Federal Drinking Water Standards (MCL) have not been found in public drinking water for most counties east of the Cascade Mountains. Triclopyr and it metabolite TCP are persistent and mobile enough to be of concern as potential ground water pollutants. Because of the properties of triclopyr and TCP, EPA (EPA RED, 1998) has expressed concern in their ground water assessment and may require that triclopyr be classified as a restricted use herbicide. However, there have been very few detections of triclopyr in well water. A total of 379 wells were sampled in four states and only five were found to contain triclopyr residues. The concentrations detected were (0.000006 to 0.00058 ppm), which is below the lifetime health advisory level for triclopyr of 0.350 ppm a.e. and below the temporary water residue tolerance for potable water of 0.5 ppm a.e. Therefore, the U.S. EPA does not currently require a restricted use classification. However, because triclopyr used in aquatic and wetland environments has a greater potential to impact both potable surface water and ground water, the EPA may require surface and ground water perspective studies in the future. Downstream surface water treatment plants located more than 2000 feet from the treatment area are not likely to experience levels of triclopyr that exceed the temporary potable water tolerance of 0.5 ppm a.e. (Ritter and Peacock, 2000). In order to avoid using water that is above the Temporary Federal Drinking Water Standard, a setback distance of 200 to 2000 feet from a water intake located in a lake or reservoir must be observed; the setback distance varies with the type of weeds treated (floating/emerged or submerged), area to be treated and the treatment rate (Garlon® 3A label). Triclopyr is not likely to be found in the water of sewage outfalls since waste water treatment plants only process water from household waste and water runoff from street level. Due to the short dissipation half-life (0.5 to 7.5 days), high levels of water exchange and dilution of triclopyr in water bodies, additional procedures for removing triclopyr from outfalls or potable water systems is probably not necessary. There are currently no methods recommended for the removal of triclopyr from wastewater outfalls and potable water systems.

According to Scott Fink (2000, personal communications) of the Spokane Department of Health: Drinking Water Division, herbicides have never been detected in surface water systems at concentrations that exceed the Federal Drinking Water Standard in any Washington State county east of the Cascades. There has never been a herbicide detection that exceeds the EPA's Drinking Water Criterion in public well water. The current temporary potable water residue tolerance for triclopyr is 0.5 ppm a.e. and the lifetime adult health advisory (HA) is 0.350 ppm. Public water supply systems are not currently required to sample and analyze for triclopyr (EPA RED, 1998). However, there have been a few cases where herbicides were found in well water at concentrations that exceed

Washington State's detection limits, triclopyr has not been found in wells from four separate states at levels that exceeded 0.00058 ppm a.e.

- **Potential impacts on recharge areas**

  Due to the limited amount of data collected, it is difficult to determine if triclopyr will have an adverse impact on sensitive well recharge areas. Triclopyr and its TCP metabolite have exceeded triggers for ground water concerns because of their extremely high mobility (K_d =0.165 to 0.975), high water solubility, depth of leaching in terrestrial field studies and relatively slow field dissipation of typically more than 4-days. However, the limited database on detects of triclopyr in wells does not allow for a current restricted use classification by the EPA (EPA RED, 1998). Due to their physical properties, triclopyr and TCP are likely to have adverse impact on surface and ground water. The soil distribution coefficients (Kd) are 0.165 to 0.975; and Kds of this magnitude would classify triclopyr as highly mobile. Since triclopyr is readily converted to TCP, TCP may also be a risk to surface and ground water. Although the EPA does not currently have a surface or ground water advisory for triclopyr, depending on the results of future surface and ground water monitoring studies, an advisory may be necessary and it may also be necessary to classify triclopyr as a restricted use herbicide. The reason that triclopyr does not have a current ground water advisory or restricted use label depends more on its current use patterns than on how it will be used in the future as an aquatic and wetlands use herbicide (EPA RED, 1998).

- **Impact of pesticide application on downstream water treatment plants**

  Recent modeling work on the effects of triclopyr on downstream water treatment plants has been conducted (Ritter and Peacock, 200). Under a worst case scenario, based on modeling the most conservative view on the triclopyr application, bed sediment type, bulk density of bed sediment, sediment-water partition coefficient, fraction of organic carbon content in sediment, plant mass in treatment area, plant water partition coefficient, longitudinal dispersion coefficient, horizontal dispersion coefficient, vertical dispersion coefficient, stream velocity on the riverbank, stream velocity in the river center, water half-life, plant and sediment half-life, setback distances and waiting periods required to ensure safety of water to be used for domestic purposes were determined. For the maximum use rate of 2.5 ppm a.e. for control of emerged weeds, the maximum potable water setback distance for application to a >16 acre reservoir is 2000 feet (Garlon® 3A label). If Garlon® 3A is applied for control of submerged weeds in ponds with a potable water intake pipe, a minimum of 21 days following application must pass before the treated water can be used for household purposes.

- **Presence of pesticide in the outfall**

  If the label restrictions are followed, the concentrations of triclopyr at water intake pipes should be less than the temporary potable water residue tolerance (0.5 ppm a.e.). Since wastewater treatment plants only process water from household waste and water runoff from street level, triclopyr from treatment of lakes, ponds, streams, and minimal outflow canals will not be present in the outfall (Jim Milton, Ecology Manager of Sewage Treatment Plant Permits, 2000).

- **Need for additional procedures to remove pesticide from the outfall**

  In cases where the concentration of triclopyr is higher than the Temporary Federal Drinking Water Standard, there have been no methods developed for the cleanup of excessive concentrations of triclopyr. The water dissipation half-life (t1/2 = 0.5 to 7.5 days) is probably short enough so that removal of triclopyr from contaminated sites is not necessary. The EPA clearly believes that high concentrations of triclopyr are not likely to occur since public water systems are not required to sample or analyze for triclopyr. Furthermore, there is no surface or groundwater advisory currently in effect for triclopyr, which has a very low mammalian toxicity. E.g., a concentration of triclopyr as high as 500 ppm a.e. on feed is unlikely to have a toxic effect on livestock animals; the residue tolerance of triclopyr on pastureland forage grasses is 500 ppm a.e. and grass hay is 200 ppm.

  Photolysis and bacteria are known to degrade triclopyr and TCP to carbon dioxide, water and organic acids. Therefore, there may be some potential for treating small amounts of water with photochemostats, chemostats or biofilms containing bacteria that are known to degrade triclopyr. Although bacteria and other microbes are known to degrade triclopyr and TCP, it is unclear from the literature sources examined which species may be most effective. It is possible that the species that degrade 2,4-D may also be effective in degrading triclopyr and TCP. This may have some potential for mitigating cases of triclopyr water pollution. Species of bacteria known to degrade 2,4-D that may also be effective in degrading triclopyr include *Acaligenes eutrophus, Arthrobacter, Bordetella, Flavobacterium, Pseudomonas* and *Xanthobacter*. However, additional work with these and other species needs to be carried out to determine the most appropriate species and feasibility of this approach.

4.2.4 Mixtures with Other Pesticides and Incidental Presence of Other Pesticides

Summary: Tank mixes are generally not permitted in Washington State. However, when liquid triclopyr products are used to control floating aquatic weeds, low levels of nonionic surfactants can improve the efficacy of liquid triclopyr products. If surfactants are used, care should be taken to use non-ionic surfactants registered for aquatic use since they have low toxicity to fish. Thickening agents like Polysar® or Nalquatic® may be of use to control drift with liquid triclopyr products that are applied to floating and emergent weeds. These thickening agents may be of further use in allowing subsurface applications to sink more deeply into the water column where they can be most effective against submerged weeds.

There are claims that combinations of triclopyr and diquat may be effective in broadening the spectrum of activity with controlling Eichhornia crassipes *and* Pistiastriotes*. Neither herbicide is effective against both species but their additive effects control both species at concentrations of 3.3 kg a.e./ha triclopyr plus 0.28 Kg diquat a.e./ha. Also the use of triclopyr plus the surfactant Kinetic® at 0.125% v/v improved the activity of triclopyr against* Eichhornia crassipes *at triclopyr rates of 0.41, 0.83 or 1.7 Kg a.e./ha (Langeland and Smith, 1993). No observations of synergism or antagonism have been seen with triclopyr. Triclopyr is one of the few herbicides, which is known to lack cumulative effects against fish and aquatic invertebrates. Triclopyr has low chronicity to fish and invertebrates. The toxicity of triclopyr to fish and invertebrates is* *similar at 24 hours, 96 hours, 21 days and 31 days (Gersitch et al, 1984, Wan et al, 1987, Mayes et al, 1984).*

Formulations of triclopyr may act in combination with other pesticides under three scenarios: 1) Applied as a mixture; 2) Broadcast in separate applications (e.g., areas where pesticides are applied for mosquito and aquatic vegetation control); or 3) Accidentally combined as a result of over-spray in marginal areas or of run-off from neighboring areas treated with different products. Herbicide mixtures may result in antagonistic, synergistic, additive or cumulative effects (same herbicide applied more than once or for which continuous exposure occurs). It should be noted that tank mixes of pesticides are not generally permitted in Washington State for control of aquatic weeds.

Because very little work has been done on the effects of pesticide combinations, it is unclear whether pesticides applied for other purposes could substantially enhance the toxicity and persistence of triclopyr.

In the State of Washington, triclopyr products are rarely mixed with other products. A number of nonionic surfactants are registered for use with water-soluble ionic herbicides like triclopyr when they are applied to floating or emergent plants. The professional researcher (Getsinger, 2000) whom we consulted with, believes that when a liquid pesticide is applied to floating or emergent vegetation that a surfactant and/or drift control agent should be used.

Only two formulations of triclopyr (Garlon® 3A and Renovate®) are typically used for the control of aquatic weeds in public waterways. Since these products are both manufactured by Dow AgroSciences, the effects of different formulations on aquatic organisms are not relevant. However, triclopyr acid (98.8% a.e.) and Triclopyr TEA (32% a.e.) have been reported to be differentially effective against *Selenastrum capricornutum* with EC_{50}s of 47 and 8.3 ppm a.e., respectively. Also triclopyr TEA (46.4% a.e. has been reported to be less toxic to bluegills LC_{50} = 413 ppm a.e.), and rainbow trout (LC_{50} = 256 ppm a.e.) than triclopyr TEA (33% a.e.) with an LC_{50} of 147 and 82 ppm a.e., respectively. This data indicates that different inert materials or lack of inert materials in some formulations may significantly alter the apparent toxicity of triclopyr. Different "inert materials" and contaminants in formulations from different manufacturing processes may interact with the pesticide to give antagonistic, additive, cumulative or synergistic effects against target species (aquatic weeds) and non-target fish and aquatic invertebrates. It is not necessary to use adjuvants with subsurface injections of triclopyr. However, a thickener is often used with liquid products to allow the treatment to sink more deeply into the water column where it can be most effective against submerged weeds; and non-ionic surfactants are recommended when the species of weed to be controlled is emergent or floating.

- **Adjuvant effects**

  When liquid triclopyr products are used to control floating or emergent weeds like alligatorweed, American lotus, purple loosestrife, waterhyacinth, water lilies or waterprimrose, the use of a non-ionic surfactant and a thickening agent are recommended. The non-ionic surfactant should be used to allow for better wetting of floating or emergent weeds and the thickening agent should be used to prevent drift. There are a number of non-ionic surfactants registered for aquatic use in Washington

State. Most surfactants should be mixed at 0.25% to 0.5% by weight of application solution when triclopyr is being applied to floating (surface) or emerged aquatic macrophytes. The toxicity of these adjuvants to bluegill, rainbow trout and *Daphnia magna* has been well documented. None of these aquatic adjuvants should be toxic to fish or aquatic invertebrates when applied at labeled rates. However, Watkins et al (1985) noted that some aquatic adjuvants have a potential to be toxic to aquatic organisms when applied in shallow water. For example: 1) If Spar-Mate® is applied at the labeled use rate to water with a depth of less than 1.5 meters, it can be toxic to bluegill sunfish. 2) If Cide-Kick®, X-77®, Formula 403®, or IVOD® are applied at the labeled use rate to water with a depth of less than 0.1 meters, they may be toxic to fish. Since the depths given are for concentrations of the adjuvant that will kill 50% of the treated animals, an additional safety factor of ~10-fold would need to be added to assure safety of the adjuvant when applied at labeled rates. Details of the toxicity and depth considerations for a number of aquatically applied adjuvants can be found in Table 8. Although adjuvants are typically considered to be "nearly inert", they are not entirely inert. However, adjuvants labeled for aquatic use should not be sub-acutely, acutely or chronically toxic to fish or other aquatic animals. Adjuvants can either enhance, diminish, or have no effect on the activity of herbicides. Because ionic surfactants may react with ionic herbicides, they should not be used with triclopyr, which has an organic acid or conjugate base as the toxic agent. Although acute aquatic testing has been done on a number of adjuvants, insufficient data exists on the toxic effects of adjuvants when mixed with herbicides and applied to the aquatic ecosystem. However, the surfactant (Kinetic®) at a concentration of 0.125% w/w improved the activity of triclopyr, TEA applied at 0.41, 0.83 or 1.7 Kg a.e./ha against *Eichhornia crassipes* (Langeland and Smith, 1983).

No particular surfactants are specified in the Renovate® experimental label or in the proposed Garlon® 3A label. Therefore, experts should be consulted prior to the use of a specific non-ionic surfactant with triclopyr for the control of floating of emergent weeds.

- **Antagonistic effects**

  Antagonism is defined as a less than additive effect when using pesticides in combination with each other. There are no specific studies that indicate triclopyr is antagonistic with other pesticides. However, ionic-surfactants must be avoided since they may react with or be antagonistic to the action of triclopyr TEA.

- **Additive effects**

  Langeland and Smith (1993) have reported that mixtures of triclopyr and diquat are strictly additive and that no interaction between these two herbicides has been observed for the control of waterhyacinth or water lettuce. However, mixtures of these two herbicides are recommended because triclopyr at 3.3 Kg a.e./ha controls waterhyacinth and diquat at concentrations as low as 0.28 Kg c.e./ha controls water lettuce.

  The label indicates that triclopyr may be used in combination with 2,4-D or Tordon 101 (picloram) for the control of woody plants in non-crop wetland sites. These combinations are probably additive in effect. However, supra-additive or synergistic effects cannot be entirely ruled out without further empirical work

- **Cumulative effects**

  Triclopyr is one of the few herbicidal products that do not appear to have any significant cumulative effects against aquatic animals. The results on fish and aquatic invertebrates indicate that the toxicity of triclopyr is similar for all exposure periods. This has been termed by some authors as a lack of chronicity (Gersitch et al, 1984, Wan et al, 1987, Mayes et al, 1984). For example, the LC_{50} for triclopyr TEA against bluegill sunfish is 161 ppm a.e. at 24 hours and 147 ppm a.e. at 48, 72 and 96 hours (Batchelder, 1973). Similar work with rainbow trout, chum salmon, Coho salmon, Chinook salmon, sockeye salmon, fathead minnows, grass shrimp and *Daphnia magna* indicate that 24-hour, 96-hour, 21-day and 31-day exposures to triclopyr did not produce LC_{50}s that are significantly different. (Tables 17, 18, 19 and 20). However, in macrophyte plants, Netherland and Getsinger (1993) have shown that triclopyr TEA is effective in controlling Eurasian watermilfoil at concentrations as low as 0.25 ppm a.e. if the exposure time is 84 hours. However, if a concentration of 2.5 ppm a.e. is used, control of Eurasian watermilfoil may be achieved after 18 hours of exposure. Conversely, triclopyr TEA appears to lack chronicity against *Selenastrum capricornutum* with the 3-, 4- and 5-day EC_{50}s all being about 45 ppm a.e. (Cowgill and Milazzo, 1989).

- **Synergistic effects**

  There are no credible reports of potential synergism of triclopyr by other pesticides. However, synergistic effects cannot be ruled out without further evidence and given the number of modes of action available for proprietary pesticides, it seems likely that at least some of them will be synergistic when combined with triclopyr TEA. Nevertheless, the surfactant (kinetic®) appears to improve the activity of triclopyr against Eichhornia crassipes in a greater than additive manner (Langeland and Smith, 1983).

4.2.5 Potential Impacts on Agriculture

Summary: The use of triclopyr TEA treated waters to irrigate crops is prohibited for 120 days after application. However, established grasses may be irrigated with triclopyr TEA treated water immediately after treatment. Triclopyr TEA should not be used to in ditches and/or canals used for irrigation purposes. There are no restrictions on using water treated with triclopyr TEA for watering livestock. In light of the 500 ppm a.e. residue tolerance on pastureland grasses it is not believed that the concentrations of triclopyr TEA permissible in potable water (0.5 ppm a.e.) or immediately after treatment with triclopyr TEA (2.5 ppm) would adversely impact animal health or residues on meat or milk.

If water use restrictions are followed as described in Section 1 and the Federal Use Labels, there should be no impact on agriculture. The proposed Garlon® 3A label (2000) does not permit the use of triclopyr to control weeds in water to be used for irrigation, or domestic water supplies for a period of time specified on the label. The water use restriction period for Garlon® 3A, at the maximum use rate of 2.5 ppm a.e. is 21 days in ponds with potable water intake pipes. For lakes and reservoirs, there is a maximum setback distance of 200 to 2,000 feet from any functioning potable water intake pipe (Ritter and Peacock, 2000). The setback distance is governed by the type of weeds being treated (floating/emerged or submerged). Treated water may not be used for irrigation for at least 120 days after treatment. There are no restrictions on the use of treated water for watering livestock and since the pastureland grass residue tolerance (500 ppm a.e.) greatly exceeds the temporary water residue tolerance (0.5 ppm a.e.) or the maximum use rate (2.5 ppm a.e.), it is unlikely that livestock health or tissue residue levels will be adversely impacted. These water use restrictions can be mitigated by residue analysis that indicates no detectable triclopyr concentrations in irritation water and concentrations or triclopyr concentrations <0.5 ppm a.e. for potable water sources. The current accepted laboratory analytical methods are immunoassays which are very sensitive.

There are strong indications that triclopyr will not persist for more than 2 weeks in lakes and reservoirs at concentrations greater than 0.5 ppm a.e. (Green et al, 1989, Petty et al, 1998). In ponds, triclopyr is unlikely to persist for more than three weeks at concentrations higher than 0.5 ppm a.e. (Petty, 1998). This data supports the three week water use restriction on ponds used as a potable water resource. So some confidence can be placed in the restrictions on the Garlon® 3A proposed label (2000).

- **Potential impacts of water on irrigation**

  The 120-day water use restriction for irrigation specified in the label and discussed above was put in place because there have not been any irrigated crop studies conducted. Irrigated crop studies are conducted to show that plants will remain healthy when exposed to irrigation water containing triclopyr at various concentrations, and to determine the residue levels that will be found in plant tissue at the time of harvest. Since these irrigated crop studies have not been conducted, a 120-day irrigation restriction has been place on waters treated with triclopyr TEA. Assuming the longest half-life (7.5 days) that has been seen for ponds treated with 2.5 ppm a.e. triclopyr TEA, concentrations or triclopyr 120 days after treatment with triclopyr TEA should be very low (e.g. 0.000038 ppm a.e.). Such low concentrations are unlikely to have adverse impact on plant health or plant residue levels at harvest. In general, broad leaf plants are susceptible to triclopyr, while grasses and grains are resistant. Triclopyr is therefore toxic to many non-target broadleaf plants, including both crops and native vegetation. Adverse effects depend on rate of application, number of applications over a confined period and the relative susceptibility of individual species.

  The use of triclopyr as a weed killer is described on both the proposed Garlon® 3A label (2000) and on the Experimental Use Renovate® label. If the water use restrictions are followed, minimal damage should occur to non-target native and crop species. However, because triclopyr is a non-specific broadleaf herbicide, it may adversely affect some crops and other non-target species exposed to irrigation water containing the active ingredient. Some crops like tobacco, grapes, vegetable crops and flowers appear to be extremely susceptible to triclopyr TEA. However, established grasses appear to be largely unaffected by triclopyr TEA.

Some species of plants may survive repeated exposure to triclopyr, if key periods where they are more or less susceptible are considered. These periods include germination (more susceptible), seedling (more susceptible), dormancy (less susceptible) and aging (less susceptible) periods. Other factors include plasticity, seed dispersal, hardiness and tolerance (Ebasco, 1993). For additional information please see Section 4.3.3.2.3. The effects of triclopyr TEA on various target and non-target plant species are indicated in Table 9. Treatment levels (6 to 9 lbs a.e./acre) used to control floating and emergent weeds, wetland associated annual and perennial weeds and woody brush would adversely impact germination and vegetative vigor of the more susceptible species of crop plant. The more sensitive crops like sunflower and onion may be affected by treatment rates as low as 0.12 to 0.005 a.e./acre.

- **Potential impacts of water used to water livestock**

  Very little of the triclopyr residues ingested by cattle and birds, are retained in the tissues. In chickens, 99% of the ingested ^{14}C-trcilopyr is excreted as triclopyr plus metabolites with the bulk of the material found in excreta (98%) remaining as unmetabolized triclopyr a.e. (Hamburg et al, 1987). In lactating goats dosed with ^{14}C-triclopyr, approximately 90% of the total residues are eliminated in the urine and 1.0% to 5.0% is eliminated in the feces. In goats, 80% to 86% of the residues in urine and feces remained as unchanged triclopyr a.e. (Puvanesarajah, 1992 and Yankovich and Bauriedel, 1976).

  If water used for watering dairy animals contains less triclopyr than mandated by the temporary drinking water residue tolerance (0.5 ppm c.e.) or the maximum use rate for the control of submerged weeds or floating/emerged weeds (6.0 lbs/acre in six inches of water = 4.4 ppm a.e.), triclopyr TEA (applied as Garlon® 3A or Renovate®) should not have an adverse impact on the animals or milk production. This conclusion is based on the pastureland residue tolerance that is 500 ppm a.e., which generally produces milk, meat, fat, kidney and liver residue levels of less than 0.01, 0.05, 0.5 and 0.5 ppm, respectively. However, evening milking can produce concentrations of triclopyr as high as 0.13 ppm a.e. and fat concentrations 24 hours after the last dosage can be as high as 0.1 ppm a.e. (EPA RED, 1998 and Puvanesarajah, 1992; Peterson, 2000 personal communication). Since the concentrations of triclopyr TEA in water will typically be 100- to 1,000-fold lower than the pastureland residue tolerance, significant health and residue impact should not occur from exposure of livestock to these concentrations (0.5 to 4.4 ppm a.e.) in their drinking water. Concentration of 10 ppm in the feed of chickens and goats produce extremely low concentrations of triclopyr in eggs, milk, muscle, fat, kidneys and liver. The magnitude of residue in animal raw agricultural commodities after exposure to triclopyr in feed at 10.0 ppm is typically very low with total residues (triclopyr plus metabolites) never exceeding 0.1 ppm [except in chicken kidneys, which are not generally considered to be edible (Hamburg et al, 1987 and Yankovich and Bauriedel, 1976)]. Since the concentrations of triclopyr in water are somewhat less (0.5 to 4.4 ppm a./e.) than those found in feed it is likely that the residue levels of triclopyr in animal products (milk and eggs) and tissues will remain low (<0.1 ppm a.e.).

- **Potential impacts of water used for agricultural sprays**

Crops other than established grasses may not be irrigated with triclopyr treated water for at least 120 days after application. This prohibition listed on the label is due to the fact that no irrigated crop studies have been submitted to support the registration of Renovate® and Garlon® 3A on aquatic and wetland weeds. Furthermore, data from studies on grasses and rice indicate that triclopyr is the only significant residue seen on these plants. To avoid adverse plant health or residue impact on crop plants, water treated with triclopyr should not be used for irrigation unless it has aged 120 days from the date of application or has been shown by analytical (immunoassay) to contain no measurable concentrations of triclopyr. EEC values in water after 120 days of dissipation are expected to be ~0.000038 ppm a.e. which should have no impact on crop plant health and residue levels. Such low concentrations have been shown to have no effect on seed germination in sensitive plants like sugarbeets and corn and that more than a 10-fold safety factor should exist for such exposures (EPA RED, 1998) (Table 9). It seems reasonable that if this restriction applies to irrigation water, that it should also apply to agricultural sprays since insufficient data exists to support the effects of triclopyr TEA treated water on plant health and tissue residue levels (Peterson, 2000 personal communications).

Another matter of concern is that one cannot determine the potential impact of previously applied materials or other pesticides in the agricultural spray. Antagonistic, additive or synergistic effects that might occur due to the presence of other pesticides, or adjuvants (surfactants, accelerator, thickeners, et cetera) have not been determined; and these effects have been known to occur with other herbicidal products. See Section 4.2.4.

- **Potential impacts on fishing and the consumption of fish**

Triclopyr is not expected to cause adverse impact on recreational or commercial fishing. The levels of triclopyr found in edible fish tissue are below the temporary residue tolerance of 0.2 ppm a.e. at all times after treatment with triclopyr TEA for a variety of game and non-game species (Petty et al, 1998; Getsinger et al, 2000; Hautman, 1998, Foster, 1998; Foster et al, 1987; Green et al, 1989 and Woodburn, 1987). Furthermore, depuration of triclopyr is rapid after exposure to triclopyr and concentrations of triclopyr in edible fish tissue drops below the limit of quantitation (~0.02 ppm a.e.) within a few days to approximately three weeks depending on the site and species tested. Subsequently, the dissipation half-life for edible fish tissue is typically less than 5 to 6 days but could range up to 12 days in catfish (Table 5). However, since the concentrations of triclopyr TEA in crayfish (4.8 ppm a.e. at application) and freshwater clams (2.49 ppm a.e. at application) exceed the temporary shellfish tolerance for 21 and 8 days, respectively at Lake Seminole, Georgia, further work is necessary to determine if a shellfish harvest restriction is necessary and how long that restriction should last. The experimental label for Renovate® currently specifies a 30-day fishing restriction and 15-day shellfish harvest restriction. However, the fishing restriction is probably not necessary and the shellfish harvest restriction may need to be extended to 21days (Green et al, 1989). Greater detail on bioaccumulation in fish and invertebrates has been reported in Section 4.2.2.4.

Ponds, lakes and wetlands treated with triclopyr at the labeled maximum use rate for the control of Eurasian watermilfoil or purple loosestrife do not cause mortality in caged or sentinel fish or shellfish that can be attributed to the direct affects of triclopyr TEA applications (Houtman et al, 1998; Foster et al, 1997; Gardner and Grue, 1993). Some sites like Lake Seminole, Georgia, Elk Grove, California, and Columbia, Missouri did not directly report fish mortality although methodology indicates that these observations were made. Therefore, since no observations of fish mortality were made at these sites, it is unlikely that significant fish mortality occurred.

Since healthy and diverse populations of phytoplankton were maintained after ponds in California, Missouri and Texas were treated with triclopyr at 2.5 ppm a.e., planktivorous fish should have adequate food supplies to maintain health and growth. The more generally nutritious green algae appeared to dominate the algae community after treatment with triclopyr. However, these green algae populations were believed to be dominant due to temperature regimens and water quality that was more favorable to green algae rather than the direct effects of triclopyr.

In the same ponds and at Moses Lake, Washington, the population of invertebrates was numerous and diverse after treatment with triclopyr TEA to control purple loosestrife. Slight changes in invertebrate numbers and diversity were generally believed to be due to normal seasonal phenological events. The population of invertebrates generally included both small forms like cladocerans, dipterans and larger forms like juvenile dragonflies and snails, which provide a diverse food source for fish of varying size.

- **Potential impact of air quality on crop plants and livestock**

Because of the manner in which triclopyr TEA (Renovate® and Garlon® 3A) are applied for the control of aquatic and wetland (non-cropland) weeds, it appears unlikely that it will have a significant impact on the air quality. However, as with all herbicides, the spray should not be allowed to drift into areas where sensitive and desirable broadleaf plants are located. Species of plant that appear to be especially susceptible are grapes, tobacco, vegetable crops and flowers. The Garlon® 3A proposed label states the following: “Applications should be made only when there is little or no hazard from spray drift. Very small quantities of spray, which may not be visible, may seriously injure susceptible plants. Do not spray when wind is blowing toward susceptible crops or ornamental plants are near enough to be injured. It is suggested that a continuous smoke column at or near the spray site or a smoke generator on the spray equipment be used to detect air movement, lapse conditions, or temperature inversions (stable air). If the smoke layers or indicates a potential of hazardous spray drift, do not spray.” Spray pressures should be kept low enough to provide course droplets. The spray boom should be kept as close to the ground or water surface as possible. Also, a thickening agent or a high viscosity inverting system should be used to prevent drift.

Even with low drift, onions and sunflowers may be adversely affected by rates of application typically used to control floating and emergent weeds (6 lbs a.e/acre) or wetland non-crop weeds (9 lbs a.e./acre). For example, treatment rates as low as 0.12 to 0.005 lbs a.e./acre lbs/acre may cause 25% damage to these sensitive crop species (EPA RED, 1998) (Table 9). These rates are exceeded even when drift is low (1% to 5%). The main methods of using Renovate® and Garlon® 3A largely preclude the effects of drift. This liquid product is either injected by subsurface methods (which precludes drift) or applied as large droplets at low pressure which mitigates the effects of drift. It is also recommended that a thickening agent be used to control drift when applying liquid herbicides to the water surface or to wetland associated weeds. However, even small amounts of drift can be an issue if many swaths are applied, and particularly if the product is applied from an aircraft (Forsythe et al, 1997).

Due to the low vapor pressure of commercial products of triclopyr (1.26x 10^{-6} mm/Hg at 25° C for the active ingredient triclopyr), they should have very little tendency to effect air quality or cause crop damage. The mode of application is usually subsurface injection for liquid formulations making drift outside the treatment area unlikely. For those cases where a boom sprayer applies a liquid formulation, as much as 1% of the application may drift out of the treatment area. It has been estimated for general herbicides that this amount of drift could have an impact if 120 swaths were applied and 1% of the applied pesticide drifted out of the treatment area on each pass. In this case, dosage levels higher than that intended for the target could accumulate downwind of the treatment area. This could cause an effect on non-target plants that may damage habitat and decrease the amount of forage available for waterfowl and fish in non-target areas (Forsythe et al, 1997). In cases where aerial application might be necessary, as much as 17% of the treatment would not strike the target area. In aerial application, drift out of the treatment area could impinge on non-target organisms at a great distance from the site of application. Depending on how much triclopyr was deposited per unit area outside the site, there could be a significant impact on non-target wild plants or crops. In addition to effects on plants, non-target sensitive terrestrial wildlife may be adversely impacted.

Odor is unlikely to be noticed except for short periods of time following application. Posting and communications requirements specified in the aquatic weed control permit should make the public aware of any potential odor problems and how long the odor problem will exist. Since there would rarely be more than one or two applications of triclopyr per water body per year in the state of Washington, any adverse impact on quality of life due to problems with odor from triclopyr applications should be weighed carefully with the impact due to the effects of poor navigability, and effects on the recreational use of the water body. Direct effects from breathing the vapor are unlikely for the general public since the acute LC_{50} for triclopyr TEA is greater than 2.6 mg/L (EPA RED, 1998). However, EPA has determined that there are potential exposures to persons involved in mixing, loading or entering treated sites after application is complete. Despite this, short-term and intermediate inhalation exposure assessments are not necessary at this time since the toxicological characteristics of triclopyr TEA are very low.

However, it has been determined that wetland (forestry) herbicides may be of particular concern to Native Americans. Forestry products are harvested by Native Americans and are used in their diets, in the making of traditional basketry, for medicinal purposes and ceremonial activities. Work is currently being conducted to determine if these exposure scenarios may affect Native Americans in a manner not reflected in the current assessment.

- **Potential impact of flooding on agriculture**

  Flooding of agricultural land with triclopyr-treated water should be a rare occurrence. When flooding occurs, dilution effects should mitigate the effects of the concentration of triclopyr. Flood irrigation, like all other forms of irrigation, is prohibited for 120 days after treatment of a water body with triclopyr TEA. Details on this irrigation restriction are discussed above under Potential Impacts of Water on Irrigation.

- **Potential impacts on aquaculture**

  Under most conditions, it is not anticipated that the use of triclopyr should have acute effects on aquaculture when the concentration of triclopyr is below 2.5 ppm a.e. The target concentration for triclopyr in aquatic use is usually 0.75 to 2.5 ppm (proposed Garlon® 3A label, 2000). Experiments conducted in lakes (Lake Minnetonka and Lake Seminole) and ponds (Elk Grove, CA, Columbia, MO and Lewiston, TX) were treated at 2.5 ppm a.e. and this is considered to be a likely treatment rate under most scenarios for the control of Eurasian watermilfoil. Such treatment rates are known to have no significant acute or chronic adverse impact on fish and to have minimal adverse impact to most invertebrates. Water would generally not be used for agricultural purposes until the concentration in the treated water body falls below the temporary residue tolerance for drinking water (0.5 ppm a.e. for triclopyr). If water used for aquaculture is taken in through surface intake pipes, the concentration will be in the range of 0.5 ppm if the setback distances specified by Ritter and Peacock (2000) are followed. Please see Section 4.2.3.2 for information on setback distances for surface water intake pipes. At this concentration even the most sensitive species of fish and invertebrate will probably not be adversely affected. For example, the 96-hour acute LC_{50} for rainbow trout is 82 ppm a.e. and the 48-hour LC_{50} for oyster embryo/larvae is ~22 ppm a.e. These concentrations provide a safety factor of more than 10-fold when the exposure concentration is 0.5 ppm a.e. Triclopyr is somewhat unusual in that the chronic toxicity (chronic LC_{50}) is not significantly different than the acute toxicity. However, the predicted chronic-MATC is 27 ppm a.e. and 2.1 ppm a.e., respectively for the most sensitive species of fish and invertebrate; and since the level of concern under this scenario is somewhat less than 1.0, it is unlikely that fish and invertebrates being raised under aquaculture conditions would be adversely impacted by triclopyr at concentrations of 0.5 ppm a.e. (Table 20).

  Because the concentrations of triclopyr that acutely effect the most sensitive commercial species run from moderately low to very high (22 ppm c.e. for eastern oyster, 82 ppm a.e. for rainbow trout), triclopyr is not likely to adversely impact cultured aquatic organisms since the exposure concentration of properly used Renovate® would typically not be higher 0.5 ppm a.e. In order to protect these commercial species from the effects of acute toxicity, the maximum concentration would have to be five to ten-fold lower than the lowest LC_{50} of 22 ppm a.e. Since the expected environmental concentration (EEC) at the point of water withdrawal would be $\leq$ 0.5 ppm a.e., fish in fish hatcheries and eastern oysters under aquaculture should be protected from the adverse effects of triclopyr (Tables 2 and 20).

  Although chronic exposure is likely to produce an MATC somewhat lower than the acute LC_{50}, inadequate research has been done to determine the MATC for most commercial species. The chronic MATC has been determined to be 41 and 35 ppm a.e. for fathead minnow and *Daphnia magna*, respectively, but chronic MATCs for rainbow trout and oysters have not been determined. However, the estimated chronic MATCs for rainbow trout and oysters are 27 and 2.1 ppm a.e., respectively, which is well above the maximum acute EEC (0.5 ppm a.e.) value likely to be found at a water intake pipe (Tables 2 and 20).

4.3 ENVIRONMENTAL TOXICITY REVIEW – TRICLOPYR TOXICITY TO THE BIOTA AND RISK ASSESSMENT

Except for their direct contact and systemic effect on aquatic macrophytes, triclopyr products are not toxic to most aquatic life. The toxicity of triclopyr TEA to algae species is very low ranging from 3.8 ppm a.e. on *Skeletonema costatum* to 496 ppm a.e. on *Ankistrodesmus* spp. The laboratory toxicity to macrophytes (*Lemna gibba* and *Lemna minor)* is also fairly low ranging from 6.5 ppm a.e. for *Lemna gibba* to 23 ppm a.e. for *Lemna minor*. While applications (2.5 ppm a.e.) to control submerged aquatic macrophytes are unlikely to have adverse impact on algae or sensitive non-target macrophytes, applications of 6 to 9 lbs a.e./acre (4.4 to 6.6 ppm a.e.) to control emerged and wetland-associated non-aquatic plants may adversely impact sensitive species of algae and aquatic macrophytes if an accidental direct over-spray of a water body with only six inches of depth occurs. Lower concentrations resulting from a direct over-spray of a water body or drainage from a sprayed field into a water body with six-foot depth (0.185 to 0.55 ppm a.e.) are not likely to have an acute effect on algae or aquatic macrophytes (EPA RED, 1998). The label indicates that triclopyr TEA (Garlon® 3A) is effective against a variety of submerged, emerged and wetland-associated terrestrial plants as well as a number of woody brush species (See section 1, Table 1 and Appendix 2). Field use of triclopyr TEA to control Eurasian watermilfoil (*Myriophyllum spicatum*) in open water ways often has little or no impact on native species such as *Najas guadalupensis, N. minor, Potamogeton nodosus*, *P. crispus, P. zosteriformis* after they have germinated and *Elodea canadensis, Heteranthera dubia* and various pondweeds (*Potamogeton* spp.) flourished following triclopyr TEA application (Netherland and Getsinger, 1993). However, higher applications of triclopyr TEA to impounded waters (ponds) may temporarily eliminate more sensitive species like *Ceratophyllum demersum*, *N. guadalupensis*, and *Elodea canadensis*. In ponds treated with triclopyr TEA for the control of Eurasian watermilfoil, the more sensitive blue-green algae forms may have been adversely impacted. However, healthy and diverse populations of algae remained in both treated and untreated ponds. The green algae and diatoms dominated the water column with the green forms like *Spirogyra*, *Cladophora*, *Mougeotia*, *Volvox*, *Closterium* and *Scenedesmus* being dominant. The macroalgae (charophytes) also appeared to be unaffected by treatment with triclopyr TEA (Petty et al, 1998) (Tables 2 and 11 to 16). All environmentally relevant species of fish appear to be tolerant to triclopyr TEA with the most sensitive stage/species being rainbow trout fry (96 hour LC_{50} = 82 ppm a.e.) and the least sensitive stage/species of fathead minnow fry (96-hour LC_{50} = 176 ppm a.e.) Triclopyr acid itself is toxic at somewhat lower concentrations (96-hour LC_{50} = 5.3 to 117 ppm a.e.) depending on fish species and the laboratory conducting the work. Since the toxicity of triclopyr TEA is so low, it is unlikely that fish will be adversely impacted by exposure to triclopyr TEA used to control submersed or emerged aquatic macrophytes. (Tables 2, and 17). Important fish to the Northwest include rainbow trout, largemouth bass, catfish, suckers, and bluegills. Field tests at Moses Lake (Washington) and Lake Minnetonka (Minnesota) and a pond in Lewisville, Texas indicate that these species are probably not affected by treatment with triclopyr TEA for the control of Eurasian watermilfoil or purple loosestrife (Getsinger et al, 2000; Houtman et al, 1997 and Gardner and Grue, 1993). Most species of aquatic invertebrates are not susceptible to the acute effects of triclopyr; 48-hour and 96-hour LC_{50}s are typically greater than 22 ppm a.e. [grass shrimp (96-hour LC_{50} = 234 ppm a.e., pink shrimp (96-hour LC50 = 281 ppm a.e.), fiddler crab (96-hour LC_{50} = >314 ppm a.e. and crayfish (96-hour LC_{50} = >103 ppm a.e.) and juvenile eastern oyster (96-hour EC_{50} = 41 ppm a.e.). There have been reports that the embryos and larvae of the eastern oyster are more susceptible to the effects of triclopyr TEA with a 48-hour LC_{50} of >18 to <27 ppm a.e. (~22 ppm a.e. = geometric mean). Since the TWA-EEC ranges between 2.3 and 6.0 ppm a.e., depending on treatment and exposure scenario, the more sensitive estuarine invertebrates may exceed the low level of concern (0.1). However, the high level of concern will not be exceeded if Garlon® 3A and Renovate® are classified and used as restricted herbicides (Tables 2, 18 and 21). However, field studies in Lake Minnetonka, and ponds located in Elk Grove, CA, Columbia, MO and Lewisville, TX indicate that a large and diverse population of invertebrates is not adversely affected by the use of triclopyr TEA for the control of Eurasian watermilfoil and purple loosestrife. Freshwater clams, red swamp crayfish and a variety of Amphipods, Diptera, Odonata, Gastropoda, Notonectidae, *Haliplus* spp., Ephemeroptera, Lestidae, *Daphnia*, Cladocera, and Chaoboridae were virtually unaffected by the use of triclopyr TEA. The rise and fall in the populations of these invertebrates can mostly be attributed to natural seasonal fluctuations (Gardner and Grue, 1997 and Foster et al, 1997).

Target macrophytes like watermilfoil and purple loosestrife will be damaged within one to 4 weeks of application. The biomass of the target species is often reduced by more than 98% after treatment with triclopyr TEA and does not re-grow significantly for one year or more after treatment. Non-target species that were in low numbers and biomass prior to treatment increased in numbers and biomass to four times the levels found in the control. However, while numbers and biomass of the native species may decrease shortly after treatment, (1 to 12 weeks), they often compete more effectively and dominate the water column by the end of the season and for a year or more after treatment (Getsinger et al, 1998; Gardner and Grue, 1996; Netherland and Getsinger; 1993 and Petty et al, 1997).

Triclopyr's effectiveness on floating emergent weeds may be improved by adding nonionic surfactants and accelerators so that triclopyr is more readily adsorbed. Triclopyr TEA products are primarily applied from boats using a spray boom or subsurface injection but may be applied from a shore vehicle using a spray boom. It is unusual for triclopyr to be applied by aircraft except for application to remote sites. Aerial application is usually avoided due to public perception that drift problems may have an adverse impact on the human habitat (Getsinger, 1999, personal communications). A drift of only 1% to 5% (3.5 to 9.0 lbs/acre in six inches of water = 2.5 to 6.6 ppm a.e.) could have significant impact on susceptible crop plants (Table 9) which are affected at the EC25 level at concentrations as low as 0.005 to 0.12 lbs a.e./acre (EPA RED, 1998). The activity of liquid formulations of triclopyr TEA may be improved by adding a thickening agent to assure that subsurface applications drop lower in the water column where they can be more effective in controlling submerged weeds or by decreasing drift when the formulation of triclopyr is applied by a spray boom.

The acute effects of triclopyr are not a major concern. The impact on the food chain should also be minimal since bioaccumulation higher than 10-fold (19 ppm a.e.) has not been seen in target plants, 1.4-fold (3.2 ppm a.e.) in non-target plants, significantly less than one-fold (<0.2 ppm a.e.) in both game and non-game fish, and 0.77 to ~2.5 in shellfish and 0.25 to 4.87 ppm a.e. in crayfish (Getsinger et al, 2000 and Green et al, 2000). Since livestock animals eliminate 88% to 98% of ingested radiation in their urine (goats) or excreta (chickens), it is unlikely that humans will be exposed to concentrations of triclopyr higher than 0.1 ppm a.e. with typical residue levels in chicken and ungulate tissue being less than the residue tolerance of 0.05 ppm for meat, and fat or 0.5 ppm a.e. for liver and kidneys (Puvanesarajah, 1992; Hamburg et al, 1987; Bauriedel, 1983 and Yankovich and Bauriedel, 1976). However, human exposure to residue concentrations higher than the current proposed shellfish residue tolerance is possible unless a shellfish harvesting restriction of 8 and 21 days is imposed on freshwater clams and crayfish, respectively.

Sub-acute effects disrupt behavior, biochemistry or respiration in fish (rainbow trout and Coho salmon). However, concentrations ranging from 72 to 288 ppm a.e. were necessary and these dosages range from about 50% to 200% of the LC_{50} (Janz et al, 1991 and Morgan et al, 1991). These concentrations are much higher than those found in the environment.

Due to the mode of action (auxin mimicry) triclopyr can take from a few days to about 4 weeks to control aquatic weeds, particularly if low rate technology is an issue. It has been suggested that much lower concentrations than are typically used for control of aquatic weeds may be effective for the control of more sensitive weeds like Eurasian watermilfoil (Netherland and Getsinger, 1993). This weed will be controlled by exposure to triclopyr TEA at 0.25 ppm a.e. for 84 hours or exposure to triclopyr TEA at 2.5 ppm for 18 hours. While 0.5 ppm a.e. provides excellent initial knock down of Eurasian watermilfoil, it was not as effective as higher rates in preventing re-growth following treatment. The lower dosages were as effective as 2.5 ppm a.e. if the exposure time was maintained at 84 hours. Although low treatment rates are recommended, it is often difficult to maintain these low concentrations for long enough exposure period to achieve control of Eurasian watermilfoil. However, using the lower treatment rates specified in the label may allow for the native species described above to effectively compete with Eurasian water milfoil and dominate the water column for 1 to 3 years after treatment with Triclopyr TEA.

Biochemical degradation of triclopyr is not extensive. Soil bacteria metabolize triclopyr TEA rapidly to TCP and TMP and subsequently to carbon dioxide, water and various organic acids. The rate of degradation may be enhanced if natural light penetrates extensively in the water column. Natural light degrades triclopyr to 5-chloro-3,6-dihydroxy-2-pyridinyloxyacetic acid and oxamic acid with a half-life of 0.6 days. The toxicity of triclopyr to microorganisms has not been adequately documented. It is possible that the same species of bacteria that readily degrade 2,4-D may also degrade triclopyr. These species include *Acaligenes eutrophus, Arthrobacter*, *Bordetella, Flavobacterium, Pseudomonas* and *Xanthobacter*. However, additional empirical work will be necessary to demonstrate which species of bacteria are most effective in degrading triclopyr.

Plants do not appear to directly metabolize triclopyr. Grasses do not readily degrade triclopyr TEA and the only significant residue found on grasses is triclopyr. Additional work would be necessary to show how aquatic weeds and plants other than grass metabolize triclopyr. Since triclopyr is not readily metabolized by grasses, the residue tolerance for triclopyr on grass forage is set at 500 ppm a.e. and the residue tolerance on grass hay is 200 ppm. Animals raised for slaughter may be fed on these feeds immediately after treatment. However, lactating dairy animals must not be allowed to graze on triclopyr TEA treated grass forage for one year after treatment (EPA, RED, 1998). While terrestrial animals do not appear to extensively metabolize triclopyr, fish and crayfish may metabolize triclopyr. Fish metabolize 10% to 20% of the adsorbed triclolopyr to TCP and TMP while crayfish metabolize about 20% to a triclopyr-taurine conjugate. Only the TCP metabolite is considered to have significant toxic impact on human consumers. However, the toxicity of TCP and TMP has been observed to be fairly high in fish with LC_{50}s ranging from 1.1 to 12.6 in salmonids to 12.5 ppm in bluegill sunfish (Wan et al, 1987 and Gorsinski et al, 1991). However, ungulates and chickens pass almost all of the consumed triclopyr through their system without changing it. Over 85% to 98% of the consumed triclopyr is found unchanged in the urine of goats and the excreta of chickens. However, typically only 20% to 30% of the residues found in milk and tissue remains as triclopyr with the rest metabolized to TCP and a polar triclopyr conjugate. Total ^{14}C-triclopyr concentrations found in milk and tissues (except liver and muscle) were ~0.1 ppm in goats. No triclopyr residues were found in muscles and less than 0.01 ppm a.e. triclopyr was found in liver. Total ^{14}C residue concentrations found in eggs and all tissues except kidney were less than or equal to 0.1 ppm. Total residue concentrations found in chicken kidneys was 0.7 ppm a.e. The goats were dosed at a feeding equivalent rate of 500 ppm a.e. and the chickens were dosed at a feeding equivalent rate of 10 ppm a.e.

(Puvanesarajah, 1992 and Hamburg et al, 1987). A more detailed discussion of the residue issue in chickens and goats can be found in section 4.2.2.4.

4.3.1 Effects and Selectivity on Aquatic Plants

Summary: Triclopyr is not highly toxic to the algae and macrophyte species tested in the laboratory. Concentrations that may be typically found in the field after treatment for control of submerged and emerged macrophytes range from 2.5 ppm to 4.4 ppm a.e. Almost all species of algae or aquatic macrophytes have EC_{50}*s that are greater than the highest expected EEC. However,* Skeletonema costatum *and* Anabaena flos-aquae *have triclopyr* EC_{50}*s of 3.8 and 4.2 ppm a.e., respectively. According to Peterson et al, (1994) (Table 13), the concentration of triclopyr used to control submersed aquatic weeds (2.5 ppm a.e.) does not inhibit the growth on any algal species at a level that exceeds EPA's level of concern (1.0). However, triclopyr applied at rates that will control emergent weeds may adversely impact the marine diatom* Skeletonema costatum *and the blue-green algae Anabaena flos-aquae. Although Peterson found that 2.5 ppm a.e. triclopyr TEA has a high risk for adverse impact to Lemna species, other authors have reported EC50s of 6.5 to 27 ppm a.e. for this species, which does not exceed the level of concern (Risk Quotient = 1.0). Recent field studies with triclopyr TEA indicate that while target species like Eurasian watermilfoil and purple loosestrife are effectively controlled by labeled use rates of triclopyr TEA, non-target species like southern naiad, pondweeds, coontail and American waterweed will not generally be affected in open waterways (rivers, and lakes). However, these species may be adversely impacted by higher treatment rates in impounded waterways (ponds) where there is little inflow or outflow of water after treatment with triclopyr TEA. These impounded waterways may be ideal for the use of triclopyr TEA at concentrations below the maximum use rate, since the dissipation of triclopyr under this scenario is relatively long (>5 days) and one can expect the concentration of triclopyr to be higher than 0.25 ppm a.e. for at least 84 hours, which should control Eurasian watermilfoil.*

Laboratory results are similar to those observed in the field when green algae, blue-green algae, and charophytes were observed to occur. During 12 weeks of observation in treated ponds, the diversity and number of blue-green species decreased, while the diversity and number of green algae and diatoms increased. The green algae appeared to dominate the water column and charophytes appeared to be unaffected by treatment with triclopyr TEA. While this was the obvious trend, the numbers of algae and the diversity of algae remained high in both triclopyr treated and untreated ponds (Petty et al, 1998). It was not entirely clear if the decreases in blue-green algae numbers and diversity was due to triclopyr treatment or due to other ecological changes in the treated ponds. While green algae flourished in treated and untreated ponds due to water quality that particularly favored their growth, there was no evidence that this growth was due to increases in the nutrient (Nitrogen/phosphorous) status of these ponds.

While the effects on fish of removing aquatic weeds from the system was not monitored, it was apparent that the numbers and diversity of the aquatic invertebrate community were not adversely affected by treatment with triclopyr. In ponds in California, Missouri and Texas, the aquatic invertebrate community remained high in population and relatively diverse with taxa ranging from small planktonic organisms (water fleas and cladocerans) to larger types (juvenile dragonflies and snails). Although the dominant organism and diversity changed somewhat during the course of the study, this was attributed to normal phenological events that occur as the seasons change.

Triclopyr is a fairly non-selective broadleaf herbicide, which also effects certain monocot plants. However, the labeled used for triclopyr in aquatic ecosystems is limited. Triclopyr TEA has been used experimentally in Washington at concentrations that range from approximately 1.5 to 2.5 ppm a.e. primarily for the control of Eurasian watermilfoil. Triclopyr TEA has also been used experimentally at rates specified as 1.0 to 2.0 ppm a.e. for the control of purple loosestrife in the Okanogan River flood plain. It is unclear where these rates came from since the emergent weed (purple loosestrife would typically be treated at 1.5 to 2 gallons/acre (1.5 to 6.0 lbs a.e./acre) according to the proposed Garlon® 3A label. However, it also has utility in the control of other species, of submerged, emerged and wetland-associated weeds including alligatorweed, waterhyacinth, parrotfeather, pennywort, water lilies, waterprimrose, and various other species of annual/perennial herbaceous weeds and woody brush. For a complete list of weed species for which efficacy is claimed please see Section 1, Table 2 and Appendix 2. Submerged weeds may be controlled at rates of 0.75 to 2.5 ppm a.e. Floating and emerged weeds may be controlled at rates of 0.5 to 2 gallons formulation/acre (1.5 to 6 lbs a.e./surface acre). Wetland (non-aquatic) broadleaf and woody brush may be controlled at rates ranging from 0.25 to 3 gallons formulation/acre (0.75 to 9 lbs a.e./surface acre). The aquatic macrophytes currently of greatest concern in the Northern Tier of States (including Washington) are *Myriophyllum spicatum* (Eurasian watermilfoil), *Potamogeton crispus* (curlyleaf pondweed), *Egeria* spp. (Brazilian elodea), Monoesius hydrilla, *Spartina alterniflora* (smooth cordgrass), *Lythrum salicaria* (purple loosestrife), *Phragmites australis* (common reed), *Nuphar* spp. and *Nymphaea* spp. (water lilies) and *Trapa natans* (water chestnut). Of these, only Eurasian watermilfoil and purple loosestrife are effectively controlled with a Renovate® or Garlon® 3A according to the labels.

Treatment under an experimental use permit at Lake Minnetonka, Lake Seminole, the Pend Oreille River, Moses Lake (Washington) and ponds in Elk Grove, California, Columbia, Missouri and Lewiston, Texas had a multi-fold purpose: 1) To control aquatic or emergent weeds (Eurasian watermilfoil and purple loosestrife); 2) Determine the persistence of triclopyr in the water column; 3) Assess the acceptability of the product label and its restrictions; 4) Assess the degree to which triclopyr drifts from the treatment area; 5) Evaluate the accuracy of a model currently used to predict triclopyr concentrations in water. It was unclear as to the level of control that was achieved at most of these sites (Getsinger et al, 2000; Petty et al, 1998; Houtman et al, 1997; Gardner and Grue, 1997 and Netherland and Getsinger, 1993). In a few field studies, triclopyr largely cleared treated areas of the target aquatic weed (Eurasian watermilfoil) when applied at concentrations of 2.5 ppm a.e. Treatment at 2.5 ppm a.e. cleared 98% of the Eurasian watermilfoil from the treated areas of the Pend Oreille River (Netherland and Getsinger, 1993). Furthermore, Eurasian watermilfoil was entirely eliminated from the treatment areas of Lake Minnetonka approximately six weeks after treatment with 2.5 ppm a.e. triclopyr TEA (Petty et al, 1998).

Non-target native species of plant competed more effectively against Eurasian watermilfoil at river and lake sites. These non-target native species dominated the waterway for up to 3 growing seasons (~36months) after treatment and included a variety of species including *Najas* spp., *Potamogeton* spp., *Elodea canadensis* and *Heteranthera dubia*. However, in impounded waterways (ponds) non-target species were often eliminated from waterways treated at high concentrations of 2.5 ppm a.e. during a 6- to 12-week evaluation period. (Petty et al, 1998). Species that could be adversely impacted in ponds treated at 2.5 ppm a.e. included coontail (*Ceratophyllum* spp.) at the Elk Grove, CA site, and American waterweed (*Elodea canadensis*) and southern naiad (*Najas guadlupensis*) at the Lewisville, TX site. In other ponds treated at the same rate, various native plant species appeared to be unaffected. For example, southern naiad was not adversely impacted by the effects of triclopyr at the Elk Grove, CA site or at the Columbia, MO site. *Chara* spp., while varying in numbers during the course of the season, was probably not directly impacted by triclopyr at the Elk Grove, CA site, the Columbia, MO site or the Lewisville, TX site. Similarly, water paspalum (*Paspaulm flutans*) was probably not directly affected by triclopyr TEA treatments at the Lewisville, TX site.

At the Moses Lake, WA site treated for control of purple loosestrife, Garlon® 3A at rates of 6% formulated product by volume, eliminated approximately 90% of the purple loosestrife in the treatment areas of two wetland sites. Purple loosestrife was visibly affected by the application of Garlon® 3A within seven days of application. However, one year after treatment over half of the purple loosestrife had recovered, based on the number of live stems present; this is a 410% increase in the number of live stems present compared with the number of live stems present after treatment. Caged sentinel duckweed plants (*Lemna minor*) were not affected adversely during the 48-hour monitoring period after treatment with triclopyr TEA.

4.3.1.1 Acute Effects on Aquatic Plants

The indicator species for aquatic toxicity in aquatic plants and algae are *Lemna gibba* (duckweed, aquatic macrophyte), *Lemna minor* (common duckweed, aquatic macrophyte), *Anabaena flos-aquae* (blue-green algae), *Selenastrum capricornutum* (green algae), *Navicula pelliculosa* (fresh water diatom) and *Skeletonema costatum* (marine diatom) (Tables 2 and 11). However, in the case of triclopyr, only one surrogate species was tested and this was the green algae *Ankistrodesmus* spp. Aquatic algae and plant species are often not tested at concentrations that exceed the expected environmental concentration (EEC). Therefore, the effects of the maximum EEC of 2.5 ppm a.e. according to the Canadian guidelines (Peterson, 1994 and 1997) is often not ascertained. All species of blue-green algae, diatoms, green algae, and macrophytes that were tested could tolerate concentrations of triclopyr TEA in excess of the maximum rate used to control submerged weeds (2.5 ppm a.e.). For example, the most sensitive species (*Skeletonema costatum* and *Anabaena flos-aquae*) had 5- to 7-day EC_{50}s that were 3.8 and 4.2 ppm a.e., respectively. However, treatment (6.0

lbs a.e./acre = 4.4 ppm a.e.) are high enough to cause adverse impact on these algal species in shallow water. In ponds of greater depth (6 feet deep), the concentration of triclopyr used to control floating/emerged species and wetland species will be much less (0.185 to 0.37 and 0.37 to 0.55 ppm a.e.) immediately after application so adverse impact from these treatments should not occur. The aquatic macrophyte tested (*Lemna* spp.) is not affected adversely by concentrations of triclopyr TEA typically used to control submerged, floating and emerged aquatic weeds.

Plants are the intended targets of aquatic herbicides containing triclopyr. Therefore, a risk assessment would not usually be conducted to determine the safety of triclopyr products on plants. A realistic level of concern may be used for aquatic plants since even a 50% reduction in growth will leave a significant amount of forage and habitat (refuge). However, except for the species discussed above, freshwater macrophytes and algae may be adversely affected by triclopyr (Renovate® and Garlon® 3A). Whether or not adverse impact occurs would depend on the characteristics of the water body. Open water bodies like lakes and rivers treated with the maximum use rate may contain healthy growths of non-target native plant species. However, in ponds where the dissipation rate of triclopyr may be much slower, these same non-target native plant species may be adversely impacted (especially in the first few weeks after treatment). Since algae species can be an important element of the food chain (Goldman and Horne, 1983), a risk quotient that is less than the level of concern (1.0) indicates that both the algae and the animals that depend on it as a primary source of food will probably not be adversely impacted in all but very shallow water bodies (RQ = EEC/EC_{50} = 0.65 = 2.5 ppm a.e./3.8 ppm a.e.). Sensitive aquatic macrophytes are also not adversely impacted by concentrations of triclopyr used to control submerged, floating and emergent plants (RQ = 2.5 ppm a.e./6.5 ppm = 0.38; 4.4 ppm a.e./6.5 ppm a.e. = 0.67). Aquatic (emergent) macrophytes are important in providing both food and habitat to fish, amphibians, aquatic invertebrates, wild birds and mammals (Frank, 1972). Therefore, this low RQ indicates that these important species will remain for utilization as habitat for aquatic animals and other wildlife. Peterson et al (1994) expressed concern that the use of a risk quotient of 1.0 as the level of concern does not provide an adequate safety margin for algae and plants. He also proposed a risk assessment schemed based on a sliding scale and had varying levels of risk including “potentially low” (<0.1), Moderate (>0.1 to <0.5), High (>0.5 to <1.0) and Very high (>1.0) (Peterson, 1994) (Tables 12 and15).

4.3.1.2 Chronic Effects on Aquatic Plants

Laboratory work to determine the chronic effects of herbicides on algae and aquatic plants is currently not conducted for the purposes of registration.

4.3.1.3 Potential Impacts of Single Versus Multiple Applications

Studies performed in both the field and laboratory indicate that algal response to triclopyr TEA formulations generally will have no significant impact on the survival and growth of algae in ponds treated at the maximum use rate for the control of Eurasian watermilfoil (2.5 ppm a.e.)(Tables 13 and 14). In ponds treated with this concentration of triclopyr TEA, the populations of algae remained healthy and diverse. However, while blue-green species like *Nostoc.* spp and *Anabaena* spp. appeared to decline in treated ponds, the green algae and diatom species generally increased in numbers in both treated and untreated ponds. The green algae species generally dominate the algal community, including filamentous forms like *Spirogyra* and *Mougeotia* as well as colonial forms like *Volvox*, planktonic forms like *Scenedesmus* and desmids like *Closterium*. Healthy and diverse populations of algae allow planktovoric forms of zooplankton to flourish and no declines in zooplankton or other aquatic invertebrates could be attributed to the direct impact of triclopyr treatments on algal populations. Pond experiments were conducted at Elk Grove, CA, Columbia, MO and Lewisville, TX and similar results were seen with algae exposed to triclopyr TEA (Table 14).

Aggressive treatment with triclopyr at concentrations from 0.25 to 2.5 ppm may eliminate Eurasian watermilfoil. However, the non-target native species like southern *(Najas guadalupenis*), *Najas minor*, pondweed species (*Potamogeton* spp.), American waterweed (*Elodea canadensis*) and water stargrass (*Heteranthera dubia*) are often not affected by treatment with triclopyr TEA in rivers and lakes (Getsinger et al, 1997; Netherland and Getsinger; 1993 and Houtman et al 1997). However, in areas untreated with triclopyr TEA, the native plant species numbers and diversity were suppressed by dense stands of Eurasian watermilfoil.

The high rate of triclopyr treatment in ponds could inhibit the growth of non-target species like coontail, Southern naiad and American waterweed. However, this was not so in all cases. For example, while triclopyr treatments inhibited the growth of Southern naiad at the Lewisville, TX sites, similar treatments at the Elk Grove, CA and Columbia, MO site appeared to have no significant impact in most native species. Other species that appeared to be unaffected in ponds treated by triclopyr TEA included *Elocharis* spp., *Chara* spp. *Lemna* spp. and water paspalum (*Paspalum flutans*). Although water paspalum, *Chara* spp. and *Lemna* spp. declined after treatment with triclopyr TEA, similar decreases in the growth of these species were observed in non-treated plots (Petty et al, 1998).

From the above results, it can be seen that aggressive aquatic herbicide treatment may create more open water for fish habitat. With triclopyr TEA or other herbicides, aggressive treatment may also improve the numbers and diversity of non-target native plants, which increases refuge areas for juvenile fish and also generally improved habitat (Kilgore et al 1987 in Ecology, 1980, 1989). In general, invertebrates are more abundant on macrophytes other than milfoil. Therefore, a community shift to other plant species may result in greater abundance of invertebrates, which would provide more food for the grazing of planktovoric fish. Therefore, in most cases where an adverse effect has occurred on fish food organisms, it has been as a result of anaerobiosis rather than a loss of habitat (Frank, 1971). Furthermore, there have been no recorded cases of anaerobiosis, due to Triclopyr TEA treatment, severe enough to cause mortality in fish and aquatic invertebrates.

Ecology (1992) suggests retaining 20% to 25% of native vegetation as fish-rearing habitat in treated areas. This also creates more open water with fewer macrophytes and increases habitat for post- and non-breeding adult fish, while at the same time allowing for increased invertebrate habitat which increases the food source for fish. This intermediate approach provides improved habitat and food source for both juvenile, sub-adult and adult fish.

Although these approaches have a large element of common sense behind them, a decrease in fish populations due to lack of sufficient macrophyte habitat is still a hypothesis (Bain and Boltz, 1992; Swingle, 1956 and Swingle, 1950). Swingle indicated that for the best forage fish to game fish ratio (3 to 6), there is an ideal areal plant cover and an ideal level of foodstuff filamentous algae. However, it was not clear what these ideal levels are and they probably vary considerably from pond to pond. Ecology's (1992) suggested value of 20 % to 25% plant cover seems to be a reasonable compromise when good experimental data is not available to support such a position. There does seem to be good evidence for the need of adequate levels of filamentous algae to support vertebrate and invertebrate populations in the field. For example, Petty et al, (1997) found that treatment of a pond in Columbia, MO with triclopyr TEA resulted in ponds dominated by filamentous green algae known to be important in the diet of ranid frog species and this was the only site where the leopard frog (*Rana pipiens*) adults and tadpoles were noted to be common.

- **Potential impact on numbers**

Field studies with both algae and macrophytes indicate that the numbers of these plants can be strongly affected by the use of triclopyr at concentrations that are typically used in the field. Getsinger et al (1997), Petty et al (1998) and Netherland and Getsinger (1993), cite field and mesocosm studies, which indicate that use of triclopyr TEA at normal field rates generally does not cause significant decreases in populations of the more important species of algae and native macrophytes. After treatment of ponds with 2.5 ppm a.e., Petty et al (1998) noted that a healthy and diverse population of algae is generally maintained. There appears to be a decline in numbers of blue-green algae like *Nostoc* and *Anabaena* while the numbers of green algae and diatom species appear to increase. It is not clear whether these population shifts are due to natural phenological cycles or the direct effects of triclopyr TEA treatment. Algal blooms can be due to the release of nutrients like phosphate and ammonia from dead and dying aquatic plants and this may lead to decreased dissolved oxygen levels, which can result in adverse impact on fish and invertebrate numbers. Although algal blooms leading to dissolved oxygen slumps were seen, these blooms and DOC slumps were similar in both control and treated ponds (Petty et al, 1998 and Houtman et al, 1998).

The numbers of target plants (*Myriophyllum spicatum*) in treated lakes and rivers generally decreased to very low levels after treatment with triclopyr TEA, the numbers of non-target native species generally increased and often flourished. Eurasian watermilfoil if present was normally eliminated from treated water bodies while Southern naiad (*Najas guadalupensis*), *Najas minor*, pondweeds (*Potamogeton* spp.), American waterweed (*Elodea canadensis*) and water stargrass increased in numbers. However, the numbers of these native species were generally depressed by dense stands of Eurasian watermilfoil in untreated control sites. At sites where water was impounded (ponds in CA, MO and TX), a number of species of native aquatic macrophyte were eliminated during the 6- to 12-week evaluation period. The species that were sometimes eliminated due to triclopyr treatment from some ponds included coontail, southern naiad and American waterweed. However, other species were either not affected by the treatment with 2.5 ppm a.e. triclopyr TEA or continued to actively grow after treatment; these species included *Elocharis* spp., *Chara* spp. and water paspalum. It is noteworthy that Southern naiad appeared to be adversely impacted in some ponds but continued to grow actively in other ponds with the same treatment regiment. In many cases, declines in population of native species of plants (e.g. *Chara* spp. and water paspalum) were considered natural phenological events not due to the effects of triclopyr TEA treatment.

- **Potential impacts on diversity**

In general, there were no clear shifts in the pattern of algae species due solely to the effects of triclopyr TEA treatments. It was noted in ponds in CA, MO and TX, that a healthy and diverse phytoplankton community was maintained throughout the 6- to 12-week evaluation period (Petty et al, 1998). While blue-green algae species were observed to decrease in treated ponds and green algae species were observed to increase in treated and untreated ponds, it was not clear whether this was due to normal phenological events that occur as the season progresses or due to some impact of triclopyr exposure. However, the presence of diverse algal forms makes it likely that phytoplankton-eating fish and invertebrates will maintain healthy populations after treatment with triclopyr TEA.

The dominant macrophytes in lakes, rivers and ponds can vary depending on the history of the water body. However, the triclopyr TEA treatments at concentrations ranging from 0.25 to 2.5 ppm a.e. eliminate Eurasian watermilfoil from treatment sites in the Pend Oreille River and concentrations of 2.5 ppm were seen to eliminate Eurasian watermilfoil from Lake Minnetonka, Minnesota and ponds in Texas. After treatment with triclopyr TEA, the dominant species at the Pend Oreille River site were seen to be American waterweed, water stargrass and various species of pondweed. However, at the Lake Minnetonka site the dominant species was seen to be *Ceratopyllum demersum*, and *Elodea canadensis* and *Potamogeton zosteriformis*. In the pond sites the dominant species after treatment varied from site to site with Southern naiad, *Elocharis* spp. and *Chara* spp. dominating at the Elk Grove (CA) site, various *Najas* species dominating at the Columbia, MO site, and *Chara* spp. and water paspalum dominating at the Lewisville, TX site. In plots that remained untreated, Eurasian watermilfoil continued to dominate the site and generally suppressed the growth of these more desirable native plants (Getsinger et al 1997; Netherland and Getsinger, 1993; Petty et al, 1998 and Houtman et al, 1997).

- **Naturally occurring re-growth and reproduction of non-noxious or non-invasive plants**

Noxious plants including, Eurasian watermilfoil (*Myriophyllum spicatum*), alligatorweed (*Alteranthera philoxeroides*), waterhyacinth (*Eichhornia crassipes)* purple loosestrife (*Lythrum salicaria*) and others are claimed on the label to be controlled. However, only watermilfoil and purple loosestrife appear to have a good field database indicative of this control. After treatment with triclopyr TEA at up to 2.5 ppm a.e., Eurasian watermilfoil has been observed to be controlled within 4 weeks at the Pend Oreille River (Washington), within 6 weeks at Lake Minnetonka (Minnesota) and within six weeks in pond sites at Lewisville, Texas.

However, within one year, approximately 30% of the Eurasian watermilfoil biomass returned to riverine treatment areas of the Pend Oreille River but virtually no Eurasian watermilfoil returned to cove areas treated with triclopyr TEA; and two years after treatment the amount of Eurasian watermilfoil biomass returning to riverine and cove treatment areas was 43% and 34%, respectively. In Lake Minnetonka approximately 50% of the Eurasian watermilfoil population had recovered in Phelps Bay but only 15% of the population had recovered in Carsons Bay. At the Lewisville, Texas site, the plots were not monitored for periods long enough to determine how rapidly Eurasian watermilfoil populations recovered.

While triclopyr TEA initially effected non-target native species in the Pend Oreille River site, the effect was much lower than on target species with 50% to 75 % of the exposed target biomass being eliminated after 4 weeks of exposure. At the Lake Minnetonka site, only 5% to 10% of the non-target native species plant coverage was eliminated after 6 weeks of exposure. Treatment with triclopyr TEA seemed to be less destructive of the native plant species than the presence of dense stands of Eurasian watermilfoil, which decreased the biomass or plant coverage of these native plants by 50% to 60%. One year after application native plant species were significantly higher than in untreated reference plots at both the Pend Oreille River site and at the Lake Minnetonka site. The plant biomass or plant cover of these native species increased by as much as 3- to 10-fold over the pretreatment biomass or plant cover. Three growing seasons after application, the biomass of native plants remained significantly higher in the Pend Oreille River in both riverine and cove treatment areas while the growth of watermilfoil was suppressed. This was attributed to the doubling of native plant species diversity and the restoration of a robust natural plant community (Getsinger et al, 1997 and Petty et al, 1998).

Triclopyr appears to be extremely selective and often spares non-target native macrophyte species even when used at concentrations as high a 2.5 ppm a.e. In the Northwest, typical species that may effectively compete with Eurasian watermilfoil after triclopyr TEA has eliminated this noxious weed include the following species: Rushes (*Scirpus* spp), cattails (*Typha* spp.) Southern naiad (*Najas guadalupensis*) Najas minor, coontail (*Ceratophyllum demersum*), pondweeds (*Potamogeton nodosus*, *P. crispus*, and *P. zosteriformis*), American waterweed (*Elodea canadensis*) and water stargrass (*Heteranthera dubia*). Native species that seem to grow particularly well in Northwest waters after treatment with triclopyr TEA include American waterweed, water stargrass and the various pondweed species (Netherland and Getsinger, 1993).

- **Post treatment plantings of non-noxious or non-invasive species**

In a general review article, Frank (1972) recommended the planting of non-noxious, and non-invasive native plants after the elimination of exotic noxious and invasive plants. However, some scientists have found efforts to reestablish native plant species are often unsuccessful. He indicated that such plantings would be competitive with the faster growing exotics once they have been eliminated. These native species can serve as both food and habitat for waterfowl, fish food organisms and fish. For a further discussion of the effect of triclopyr on numbers and diversity of aquatic animals, please see Section 4.3.2.3.

It is noteworthy that the biomass or frequency of Eurasian watermilfoil decreases and the biomass or frequency of native macrophytes increases. However, the total biomass or frequency of combined milfoil and native aquatic plants appears to remain about the same. This is expected since the carrying capacity of any treated water body remains the same while removal of pest species makes way for other plants to replace the pest species through more effective competition.

- **Effects on aquatic plants: potential impacts of single versus multiple applications**

There has been no significant experience with multiple applications of triclopyr TEA for the control of submerged, emerged and floating weeds. Although triclopyr can be applied at rates of <2.5 ppm a.e. and <2-gallons formulation/acre for the control of submerged and floating/emerged weeds, not more than 2.5 ppm a.e. or 2 gallons formulation/acre may be applied per annual growing season if the proposed Garlon® 3A Label is followed. Triclopyr is not believed to be cumulative in effect. Therefore, if the seasonal application rate is applied in one or several applications, no significant difference in the overall effect on aquatic plants should occur. However, exposure of Eurasian watermilfoil to 0.25 ppm a.e. triclopyr TEA for 84 hours should give equivalent control as exposing this species to 2.5 ppm a.e. triclopyr TEA for 18 hours.

4.3.1.4 Effects on Endangered Plant Species

The current literature does not discuss the effects of triclopyr on endangered species. However, a few general comments can be made. Renovate® or Garlon® 3A (liquid triclopyr TEA) is normally applied at or below the water surface or as close to the water or ground surface as possible; thus accidental "drift" exposure to upland vegetation during application would be minimal with the exception of emergent or wetland aquatic plant communities bordering the treated area. If any proposed "sensitive" plants or candidate species under review for possible inclusion in the state list of endangered or threatened species occurs along the banks of waterways to be treated with triclopyr products, the applicator should leave a protective buffer zone between the treated area and the species of concern (Ecology, 1989). Sensitive upland plant species could potentially be damaged if treated water was improperly used for irrigation or extensive flooding from drainage canals treated with triclopyr TEA for the control of terrestrial or emergent weeds growing on the ditchbanks. This is likely only if the plants are exposed before significant herbicide dissipation has occurred. Use of treated water for irrigation will normally be prohibited for 120 days after treatment with Renovate® or Garlon® 3A or until an acceptable analytical method (immunoassay) shows the concentration of triclopyr has decreased below the limit of detection in water. To protect endangered aquatic plants, some knowledge must be gained on the toxicity of triclopyr to these plants, or triclopyr must not be applied in areas that will adversely impact the habitat or population of these plants. In the case of threatened aquatic plants, the Endangered Species Act does not allow for the control of noxious weeds to take precedence over the protection of endangered species. However, if conditions indicate that removal of noxious weeds will improve habitat for threatened/endangered plant species, removal of the noxious species by chemical or other means should be considered. The permit for treatment of water bodies to control noxious or invasive plants may be denied or amended if "Ecology" believes that populations of endangered or threatened plants may be adversely impacted by treatments to control these weeds (McNabb, 1999 and Dorling, 1999 personal communications).

Endangered plant species in the State of Washington that are either fully aquatic, palustrine or riparian are as follows: Ute Ladies' Tresses, Golden paintbrush, Nelson checker mallow (terrestrial species); water howellia, marsh sandwort or *Lobelia* spp. (aquatic species) (Table 23).

4.3.1.5 Risk Analysis for Aquatic Species of Plants

It is not standard procedure to conduct a Risk Assessment with a herbicide for aquatic plants and algae. Since blue-green algae are often important for nitrogen fixation, it is important that the risk be low for these species. In general, the risk is low to moderate for all species of aquatic plants that have been tested (Table 15). Treatment for the control of submerged plants (2.5 ppm a.e.) or floating and emerged plants (6 lbs a.e./acre = 0.185 to 0.36 ppm) that are in fairly deep water (≥6 feet) should not have significant impact on algae or aquatic macrophytes. The highest EEC expected from these scenarios will not exceed the EC_{50}s for either the most sensitive species of algae (*Skeletonema costatum*) or for the macrophyte test species (*Lemna gibba* and *Lemna minor*). Since the risk quotient for these species is below the level of concern (RQ = 2.5 ppm a.e./3.6 ppm a.e. = 0.69 for *Skeletonema costatum*; RQ = 2.5 ppm /6.5 ppm a.e. =0.38 for *Lemna gibba*), the risk to non-target algae and macrophytes is acceptable. Field studies indicate that almost all species of algae are not adversely impacted by exposure to triclopyr TEA and that healthy and diverse plankton communities are maintained after exposure to triclopyr TEA at 2.5 ppm a.e. (Petty et al, 1998). It is unclear, however, whether population shifts from blue-green to green algae and diatoms is due to normal phenological events during the season or to some subtle ecological effects due to the exposure of these algal species to triclopyr TEA. Furthermore, while many non-target native macrophytes are unaffected by exposure to triclopyr TEA in rivers or lakes, exposure of these species in water impoundment situations (ponds and possibly small reservoirs) to higher concentrations of triclopyr TEA (2.5 ppm a.e.) may temporarily eliminate the more sensitive species like coontail, southern naiad or American waterweed from the impoundment (Netherland and Getsinger, 1993; Houtman et al, 1998 and Petty et al, 1998).

Treatment of shallow water bodies (≤6 inches) with triclopyr TEA to control floating or emergent weeds could lead to water concentrations (4.4 ppm a.e.) that are high enough to adversely impact the more sensitive diatoms and blue green-algae. Since the risk quotient under this scenario is >1.0 the level of concern is exceeded for these algal groups and an adverse impact to this segment of the biota can be anticipated; (RQ = 4.4 ppm a.e./ 4.2 ppm a.e = 1.1). Species of invertebrate or phytoplanktivorous fish that depend on blue-green algae or diatoms may be adversely impacted due to nutritional considerations under this scenario. Under this scenario, it is not anticipated that aquatic macrophytes would be adversely impacted since the level of concern for this segment of the biota is not exceeded; RQ = 4.4 ppm a.e./6.5 ppm a.e. = 0.68). However, while non-target native macrophytes found in rivers and slow moving lake water are not likely to be impacted, these macrophytes may still be adversely impacted in water impoundments (ponds and small reservoirs). Such effects on macrophytes have the potential to decrease the amount of refuge area and general habitat for smaller fish and wildlife associated with wetland areas.

4.3.2 Effects of Triclopyr on Aquatic Animals

*Summary: Triclopyr TEA is generally safe to fish, free-swimming aquatic invertebrates, and benthic invertebrates when the EC_{50}/LC_{50} is compared to typical 4-day time weighted average expected environmental concentration (TWA- EEC). However, when the toxicity of triclopyr is compared to other pesticides, it is classified according to the U.S. EPA Ecotoxicological Categories as slightly toxic (LC_{50} = >10 to 100 ppm) to embryo/larval and juvenile eastern oyster (*Crassostrea virginica*) rainbow trout (*Onchorhynchus mykiss*), tidewater silverside (*Mendia beryllina*), chum salmon *(Onchorhynchus keta) and fathead minnow (*Pimephales promelas*). However, triclopyr TEA is classified as practically non-toxic (LC_{50} >100 ppm) to bluegill sunfish (*Lepomis macrochirus*), other salmon species (*Onchorhynchus *spp.),* Daphnia magna*, grass shrimp (*Palaemonetes pugio*), pink shrimp (*Penaeus durorarum*), fiddler crab (*Uca pugialtor*) and red swamp crayfish (*Procambarus clarki*). In general, triclopyr TEA can be considered to have very low toxicity to environmentally relevant fish and aquatic invertebrates. Triclopyr TEA* *appears to be extremely safe for use in the presence of threatened and endangered salmonid game-fish.*

Triclopyr TEA appears to be safe for use in aquatic ecosystems. When comparing typical expected environmental concentrations (EEC) of triclopyr with laboratory LC_{50}s, the highest concentration that may be encountered immediately after application (2.5 ppm a.e. for control of submerged weeds or 4.4 ppm a.e. for control of floating and emerged weeds in shallow water) may affect more sensitive species. Fish and non-mollusk species would not be adversely impacted by these concentrations of triclopyr TEA. For example, the most sensitive fish species is rainbow trout with a 96-hour LC_{50} of 82 ppm a.e. and the most sensitive non-mollusk invertebrate is the red swamp crayfish with a 96-hour LC_{50} of >103 ppm a.e. Since these species have LC_{50}s that are >10-fold greater than the EEC that occurs immediately after application, it is not likely that they would be adversely impacted by the effects of triclopyr TEA. However, the most sensitive mollusk is the embryo larval stage of the eastern oyster with a 48-hour EC_{50} for improperly developed embryo/larvae of 22 ppm a.e. Since the risk quotient generated from this LC_{50} and the lowest initial EEC is greater than the low level of concern (0.1), this segment of the biota may be harmed by exposure to triclopyr TEA. However, since the risk quotient is not higher than the high level of concern (0.5), this segment of the biota will probably not be adversely impacted if triclopyr is classified and used as a restricted use aquatic herbicide ($RQ = EEC/EC_{50} = 4.4$ ppm a.e./22 ppm a.e. = 0.2). Some concern has been expressed that the eastern oyster in not an appropriate species to use in evaluations of risk for compounds that may not be used legally in estuaries. Furthermore, any concentration of triclopyr TEA entering an estuary would be greatly diluted by both untreated river/creek water and untreated sea water from the tidal action.

Other mollusks that occupy fresh water may not be entirely safe from the effects of triclopyr TEA even if a 4-day TWA-EEC (2.1 to 3.7 ppm a.e.) value is used to generate the risk quotient. In this case, the low level of concern (0.1) will still be exceeded (RQ = 3.7 ppm a.e./22 ppm a.e. = 0.17).

*The chronic toxicity (MATC) for triclopyr is also low. The most sensitive invertebrate species (eastern oyster) has a predicted long-term MATC of 2.1 ppm a.e. and the most sensitive fish species (rainbow trout) has a long-term MATC of 27 ppm a.e. Fish species will not be affected by triclopyr TEA at 4.4 ppm even if triclopyr is assumed not to degrade over a 31-day exposure period or if triclopyr TEA is assumed to lack chronicity even in an early life-stage study. At this initial concentration for controlling floating and emerged weeds in shallow water the chronic level of concern (1.0) will not be exceeded; (RQ = 4.4. ppm a.e./27 ppm = 0.16). Since the chronic level of concern is not exceeded using these strenuous assumptions, it is not likely that triclopyr TEA will have adverse impact on the reproduction and growth of the fish biota. However, even if triclopyr TEA is assumed to degrade and not exhibit chronicity, the most susceptible estuarine invertebrates (mollusks) may be adversely impacted. For example, since the 21-day TWA-EEC for a 4.4 ppm a.e. application is 1.94 ppm a.e., the chronic level of concern (1.0) will not be exceeded; RQ = 1.94 ppm a.e./2.1 ppm = 0.92. Since the chronic level of concern is not exceeded, this segment of the biota will not be at risk if these more liberal assumptions are made. If more conservative assumptions are made, as was done with fish, the chronic level of concern will be exceeded and this segment of the invertebrate biota would be judged to be adversely impacted as to their reproduction and growth; RQ = 4.4. ppm/2.1 ppm a.e. = 2.1. However, if this apparently very sensitive and perhaps not environmentally relevant species (*Crassostrea virginica*) is excluded, the* *red swamp crayfish yields a chronic risk quotient that is below the chronic level of concern since the predicted long-term MATC would be ~10 ppm a.e. (103 ppm a.e/10.7). Using this predicted long-term MATC, the level of concern would not be exceeded; RQ = 4.4. ppm/10 ppm a.e. = 0.44. Therefore, free-swimming and benthic crustaceans would not be adversely impacted as to reproduction and growth.*

Tests were not done on salmon smolts to determine if exposure to triclopyr allowed smolts to survive a subsequent seawater challenge or interfered with the ability of these species to migrate. However, data indicate that concentrations of ~200 ppm Garlon ® 3A (72 ppm a.e.) will adversely affect Coho salmon fry. Fortunately, such high concentrations are clearly not environmentally relevant. However, concentrations that were approximately half the LC_{50} *produced threshold changes in the behavior of rainbow trout while concentrations of twice the* LC_{50} *were necessary to produce a significant avoidance response (Morgan et al, 1991). Furthermore, concentrations up to 50% to 80% of the acute* LC_{50} *had no impact on typical measures of physiological stress in Coho salmon including no effects on the haematocrit, leucocrit, oxygen consumption, plasma glucose levels and plasma lactate levels (Janz et al, 1991). It is therefore unlikely that sub-lethal concentrations of triclopyr TEA will have a measurable short-term impact on salmonids.*

Field studies indicate that treatment with triclopyr TEA to control Eurasian water milfoil or purple loosestrife has no significant acute or chronic impact on free-swimming and benthic macro-invertebrates. No decrease in numbers or diversity of aquatic macro-invertebrates found in the field could be attributed to the direct affects of triclopyr TEA. Invertebrates that are typically found in similar numbers in both treated and untreated plots include Amphipoda, Diptera, Odonata, Gastropods, Notonectidae, Haliplus *spp., Ephermoptera, Lestidae,* Daphnia *spp., Cladocera and Chaoboridae. The rise and fall in the populations of these invertebrates can generally be attributed to natural seasonal fluctuations.*

Field studies with fish are minimal. Data with sentinel organisms (caged fish) indicates that rainbow trout adjacent to areas treated for control of purple loosestrife and bluegill sunfish, largemouth bass and brown bullhead in water treated for Eurasian watermilfoil control were not adversely impacted by triclopyr TEA. Mortalities that were seen with these species were due to decreases in the dissolved oxygen content of the water body (Petty et al, 1998; Gardner and Grue, 1996; Foster et al, 1997 and Houtman et al, 1997). Similar fish mortalities were seen in both treated and untreated water bodies. Where amphibian surveys were taken, Rana pipiens *adults and tadpoles were common in both treatment and control ponds.*

Sensitive, endangered and threatened species of aquatic animals that may need protection through mediation include Coho salmon, chum salmon (summer chum), Chinook salmon, sockeye salmon, bull trout, steelhead trout, cutthroat trout, Coastal cutthroat trout, Olympic mud-minnow, mountain sucker, lake chub, leopard dace, Umatilla dace, and river lamprey. Other species which may need protection within Puget Sound, the San Juan Islands, and the Strait of Juan de Fuca east of the Sekiu River are Cherry Point Herring, Discovery Bay Herring, and South Pacific cod. However, in general, the reviewed data indicates that even endangered fish species are not likely to be adversely impacted by treatment with triclopyr TEA.

Triclopyr applications to fully aquatic (lentic and lotic) systems are unlikely to be toxic to most aquatic animals but may be toxic to some aquatic animals (Tables 2, 16 and 17). Triclopyr will generally be safe to the most ecologically relevant species. For example, no fish species appear to be adversely impacted by the effects of triclopyr TEA. Even the most sensitive species tested (rainbow trout) with a 96-hour LC_{50} of 82 ppm a.e. is not likely to be affected by the highest concentrations of triclopyr TEA that will be typically encountered in the environment. These concentrations would be 2.5 ppm a.e. for triclopyr used to control submerged weeds and up to 4.4 ppm a.e. for triclopyr TEA use to control floating and emerged weeds in shallow water.

However, while triclopyr TEA is not toxic to free-swimming and sediment-dwelling crustaceans, it may have a low level impact on estuarine mollusks like the eastern oyster since the EC_{50} ranges from 22 to 42 ppm a.e. for this species. While the highest exposure concentration of triclopyr TEA (2.5 to 4.4 ppm a.e.) is not likely to adversely impact 50% of the animals exposed at this rate, the level of concern for acute aquatic impact (0.1) is exceeded by the higher concentrations of triclopyr TEA that might be encountered; RQ = 4.4 ppm/ 22 ppm a.e. = 0.2. However, since the high level of concern (0.5) is not exceeded by this exposure concentration, labeling and using triclopyr TEA as a restricted use herbicide will probably prevent species with similar susceptibility from being adversely impacted.

Triclopyr and its formulations have little tendency to bioaccumulate in fish, crayfish and freshwater clams. The bioconcentration factor with these classes of organisms has been seen to be <1.0, $\leq$2.0 and <1.0 ppm. The concentrations of triclopyr TEA in edible fish tissue usually is less than <0.03 ppm a.e. and was always below the temporary residue tolerance of 0.2 ppm a.e. (Petty et al, 1997; Getsinger et al, 2000 and Green et al, 1989) However, the concentrations in the tissues could be as high as 4.87 ppm a.e. in crayfish and 2.49 ppm a.e. in freshwater clams. Dissipation of triclopyr to levels below the temporary shellfish residue tolerance of 0.2 ppm could take 21 and 8 days, respectively in crayfish and freshwater clams (Green et al, 1989). It is not likely that a fishing restriction is necessary to protect the public from exposure to triclopyr from eating fish. However, a shellfish harvest restriction of up to 21 days may be necessary. The current fishing restrictions specified in the Renovate® experimental label is 30 days and the current shellfish harvest restriction is 2 weeks. Biconcentration and residue levels in fish tissue, aquatic plants, terrestrial plants, and livestock is discussed in much greater detail in sections 4.2.2.4 and 4.2.5.

Triclopyr TEA may be applied in a water carrier or as an invert emulsion through boom trailing hoses carrying nozzle tips to apply the dilute spray below the water surface to ensure adequate coverage and control of submerged aquatic weeds. Triclopyr may also be applied by spraying the water surface with triclopyr mixed with a surfactant in 20 to 200 gallons water/acre to control floating and emerged weeds. For the control of wetland associated annual and perennial broadleaf weeds and woody brush, triclopyr TEA should be mixed with a surfactant in enough water to give uniform and complete coverage of plants to be controlled. While triclopyr is combined with other herbicide products in some cases, this is not normal in Washington State. It has been suggested that triclopyr TEA may be combined with diquat for the control of waterhyacinth and water lettuce, which are both floating plants (Langeland and Smith, 1993). The proposed Garlon® 3A label states that "For control of woody plants, use Garlon® 3A at the rate of ½ to 1 gallon in water to make 100 gallons of spray solution or Garlon® 3A at ¼ to 1 gallon may be mixed with ¼ to ½ gallon of 2,4 D 3.8 lb amine or low volatile ester of Tordon® 101

Mixture herbicide and diluted to make 100 gallons of spray solution. Apply at a volume of 100 to 400 gallons of total spray per acre depending on size and density of woody plants. Coverage should be thorough to wet all leaves, stems and root collars." Herbicides should be combined with a nonionic surfactant for the control of floating/emerged weeds and wetland-associated non-aquatic weeds. A surfactant is not necessary for the control of submerged weeds but a thickener or invert emulsion should be added to control drift and allow the herbicide to sink deeper into the water column where it will be more effective against submerged weeds.

There have been no documented cases where triclopyr has been shown to be truly synergistic. However, the surfactant (Kinetic®) appears to improve the activity of triclopyr TEA against *Eichhornia crassipes* in a greater than additive manner (Langeland and Smith, 1983). Although antagonism has not been identified for combinations of triclopyr and other agricultural products, ionic-surfactants must be avoided since they may react with or be antagonistic to the action of triclopyr TEA. There has been one reported case of additive effects of triclopyr TEA with diquat when they are combined to control waterhyacinth and waterlettuce. There also do not appear to be any cumulative effects with triclopyr, particularly against animals where the effects of 24-hour triclopyr exposure is the same at longer exposure times (96 hours, 21 days and 31 days). This lack of chronicity indicates that true chronic effects may not occur and that the first few hours of exposure may be responsible for the production of all effects including those on reproduction and growth that typically do not immediately manifest themselves. More detail on the effects of triclopyr and other pesticides as synergistic, antagonistic, cumulative or additive effect agents can be found in Section 4.2.4.

No sub-acute effects have been noted at concentrations of triclopyr likely to be encountered in the environment due to the exposure to triclopyr. Experimental data indicate that at concentrations of ~200 ppm Garlon® 3A formulation, Coho salmon fry will be adversely affected. Fortunately, such high concentrations are clearly not environmentally relevant. However, concentrations that were approximately half the LC_{50} produced threshold changes in the behavior of rainbow trout while concentrations of twice the LC_{50} were necessary to produce a significant avoidance response (Morgan et al, 1991). Furthermore, concentrations less than 50% to 80% of the acute LC_{50} had no impact on typical measures of physiological stress in Coho salmon including no effects on the haematocrit, leucocrit, oxygen consumption, plasma glucose levels and plasma lactate levels (Janz et al, 1991). It is therefore unlikely that sub-lethal concentrations of triclopyr TEA encountered in the environment will have a measurable short-term impact on salmonids. However, it has been suggested that very low concentrations of herbicides encountered in the environment may have subtle adverse impacts on fish and other animals, which may render them more susceptible to predation, disease and environmental assault. It is possible that the lower dosages encountered in the environment may cause pathological conditions undetectable by standard behavioral observations and necropsy but still of importance in interfering with key factors in animal physiology. However, most of these effects can be considered minimal in absence of environmental assault from sources other than the presence of triclopyr at typical expected environmental concentrations (EECs). Typical EEC concentrations are ~2.5 ppm a.e. when submersed aquatic weeds are being controlled and possibly up to 4.4 ppm a.e. when floating/emerged weeds are being controlled in shallow water. To discover the long term effects of triclopyr at environmentally relevant concentrations would require the conduct of multigenerational laboratory experiments.

Accelerators and thickening agents are rarely used with herbicides sprayed directly on the surface of a water body to control submerged weeds, but some applicators and scientists believe that surfactants like CideKick® and X-77® improve effectiveness and should be used with triclopyr products when surface (floating) weed control is necessary (Getsinger, 2000 personal communication). A thickener like Nalquatic® or Polysar® will often be used to allow a subsurface application to sink down into the water column where it will be most effective against rooted aquatic macrophytes. If the herbicide is sprayed on, thickeners also control potential drift. Although all adjuvants registered for use with aquatic herbicides should be safe to fish and other aquatic animals when used according to the label, they are not without risk to aquatic life (Watkins et al, 1985). Their 96-hour toxicity (LC_{50}) ranges from 0.96 mg/L to > 1000 mg/L. In lakes and ponds with reasonable depth, dilution should prevent toxic effects from occurring due to the use of adjuvants. This is particularly so if a spot or margin treatment is used. A more detailed discussion of the effects of adjuvants can be found in Section 4.2.4 and in Table 8. Care should be taken that only non-ionic surfactants are used since ionic surfactants may react with triclopyr to decrease its effectiveness or damage sensitive animal biota.

4.3.2.1 Acute Effects on Aquatic Animals

- **Acute effects on fish**

  Toxicity information indicates that commercial products of triclopyr have limited acute toxicity to most species of fish tested (Tables 2 and 16); that is, they have LC_{50}s greater than 82 ppm a.e. for all species tested that are considered to have high commercial or recreational value. Triclopyr has a 24- to 96-hour LC_{50} that ranges from ~82 to ~170 ppm a.e. for all the species of salmonid tested. These include rainbow trout, Coho salmon, Chinook salmon, sockeye salmon, chum salmon and rainbow trout. Since all species were tested in the free-swimming fry to fingerling stage, no conclusions can be drawn about the acute effects of triclopyr on eggs, embryos and sac-fry of these test species. However, in general, triclopyr TEA has been seen to lack chronicity in its effects on fish species. For example, the LC_{50} for fathead minnow at 4 and 31 days was found to be 86 and 52 to 81 ppm, respectively. Rainbow trout also exhibited a lack of chronicity with 1, 2, 3 and 4-day LC_{50}s of 165, 157, 151 and 151 ppm a.e., respectively. This lack of chronicity can be seen in bluegills, tidewater silverside fathead minnow and all species of salmonid tested.

  Based on these LC_{50}s, triclopyr can be placed in the ecotoxicological risk categories as follows: slightly toxic (LC_{50} = >10 to 100 ppm a.e.) for tidewater silverside, rainbow trout, chum salmon, Chinook salmon and fathead minnow and practically non-toxic (LC_{50} = >100 ppm a.e.) for bluegill sunfish, Coho salmon, and sockeye salmon. These risk category classifications do not mean triclopyr will or will not have an adverse impact to fish when they are exposed to the expected environmental concentration. This determination of risk compares the general toxicity of triclopyr with other registered pesticides; based on this comparison, triclopyr is slightly toxic to practically non-toxic for all species of fish tested.

  The application rate for triclopyr in the United States typically ranges from 0.75 to 2.5 ppm a.e. to control submerged aquatic macrophytes; and can range from 1.1 to 4.4 ppm a.e. in water where triclopyr TEA has been sprayed at 1.5 to 6.0 lbs a.e./acre for the control of floating and emergent aquatic weeds. The typical maximum use rate in the United States is around 2.5 ppm a.e. for both whole pond treatments as well as lake and river treatments (Getsinger et al 2000; Petty et al, 1998; Green et al, 1989 and Getsinger et al, 1997; Netherland and Getsinger, 1993). Therefore, fish biota should be largely unaffected by normal treatments with virtually no mortality occurring even when the most sensitive species are present.

- **Acute effects on aquatic invertebrates**

  Toxicity information indicates that the commercial products of triclopyr have a limited acute toxicity to most species of aquatic invertebrates tested (Tables 2, and 17). That is, the LC_{50} is >103 ppm a.e. for all species of aquatic arthropod (crustacean) tested. At these concentrations triclopyr TEA is classified as practically non-toxic. The effects of triclopyr on the mollusk (eastern oyster) is 3 to 5-fold higher than for arthropods. However, the toxicity of triclopyr TEA is still very low classifying it as slightly toxic. These risk category classifications do not mean triclopyr will or will not have an adverse impact to invertebrates when they are exposed to the expected environmental concentration. However, since the LC_{50}s for both arthropods (crustaceans) and mollusks is considerably higher than the typical EEC-value, acute toxicity to invertebrate species is not likely. Furthermore, in estuarine species like eastern oyster, significant dilution of triclopyr TEA concentrations should occur prior to and after this pesticide enters an estuary making it even less likely that these estuarine species will be adversely impacted.

  The application rate for triclopyr in the United States typically ranges from 0.75 to 2.5 ppm a.e. to control submerged aquatic weeds and can range from 1.1 to 4.4 ppm a.e. in water where triclopyr TEA has been sprayed at 1.5 to 6.0 lbs a.e./acre for the control of floating and emergent aquatic weeds. Typical maximum use rate in the United States is around 2.5 ppm a.e. for whole pond treatments, lake and river treatments (Getsinger et al, 2000; Petty et al, 1998; Green et al, 1989 and Getsinger et al, 1997). Therefore, invertebrate biota should be largely unaffected by normal treatments with virtually no mortality occurring even when the most sensitive species are present. However, since at the higher possible exposure rates, the risk quotient will be higher than 0.1 and lower than 0.5, triclopyr TEA should be classified and used as a restricted use herbicide. Under these restricted use conditions, triclopyr TEA would probably not have significant adverse impact against the invertebrate biota.

  It is possible that triclopyr TEA will have adverse impact on the more sensitive benthic invertebrates even if further analysis is conducted. However, depending on half-life considerations for triclopyr and the manner in which triclopyr is applied, it may prove to be safe to the in-faunal sediment biota like mollusks (eastern oyster). The concentrations of triclopyr found in water shortly after treatment can vary considerably depending on the treatment rate, rate of degradation, and mass of water movement through the treatment area. For example, triclopyr TEA used at 2.5 ppm a.e. in a variety of situations has been observed to have a variable half-life. These half-lives can be less than 1 day in open areas of Lake Seminole (Georgia) and the Pend Oreille River (Washington) but are more typically ~4 or 5 days in protected areas of Lake Seminole, Lake Minnetonka (Minnesota), and ponds of Columbia, Missouri and Lewisville, Texas. The longest half-life (7.5 days) was observed in a pond in Elk Grove, California. Under the above circumstance, the concentrations of triclopyr TEA can be less than 0.2 ppm a.e. within 3 days of application or have concentrations that remain higher than 2.0 ppm a.e. three days after application. More detailed discussion of the levels of triclopyr found in both water and sediment can be found in Sections 4.2.2.1 and 4.2.2.2. For a determination of risk see Section 4.3.2.5.

The exact toxicity categories may not be of great importance since the evaluation presented here does not constitute a risk assessment, and exposure to triclopyr is likely to be negligible for most species even though potential exposure concentrations exceed the level of concern in the more sensitive species tested. The most sensitive species appear to be benthic and sediment invertebrates mollusks. The toxicity of triclopyr TEA to these species has been discussed extensively in early paragraphs of this section.

When environmental concentrations dramatically exceed the level of concern with the most sensitive species, the use of the compound would not be acceptable unless mitigating factors could be considered. Fortunately, whole pond applications are not considered to be a typical exposure scenario. The most typical exposure scenario is a spot treatment in lake or river (2.5 ppm a.e.). Under these scenarios, one would generally expect concentrations of triclopyr to dissipate in typical Northwest waters to time-weighted average EEC levels of 1.35 to 0.85 in 48 to 96 hours; the non-time weighted EEC under this scenario would be 0.625 to 0.16 ppm a.e. At these concentrations, the eastern oyster with an EC_{50} of 22 to 41 ppm a.e. is not likely to be affected adversely by triclopyr TEA. However, at the higher use rates (4.4 ppm a.e.) used for control of floating and emerged weeds, TWA-EEC of 2.4 to 1.5 ppm a.e. would be expected. The degradation of triclopyr assuming a <1-day half life in northwestern waters is a useful mitigation assumption only if the chronicity of triclopyr TEA is assumed to be high. However, chronicity is not believed to be a significant factor for animals exposed to triclopyr TEA. Therefore, for the most susceptible species to be protected, triclopyr TEA would have to be used as a restricted use herbicide. A formal risk assessment in Section 4.3.2.5 supports the conclusions in this toxicity review.

4.3.2.2 Chronic Effects of Triclopyr on Aquatic Animals

- **Chronic effects on fish and amphibians**

To this date, the amount of chronic or early life-stage effect data for triclopyr on aquatic animals (fish) is rather minimal (Tables 2, 10, 18 and 20). The only chronic fish study done with Triclopyr TEA was a 31-day early life-stage study with fathead minnow.

Early life-stage (egg to fry) toxicity of triclopyr TEA was investigated with the fathead minnow. After a 31-day exposure, the no observed effect concentration (NOEC), maximum allowable toxic concentration (MATC) and lowest observed effect concentrations (LOEC) were 33, 41 and 52 ppm a.e., These values are based on the difference in standard length between control fish and treated fish after 31 days of exposure.

Even the highest EEC at the time of application (2.5 to 4.4 ppm) should not chronically impact fathead minnow since it is well below the chronic MATC concentration of 41 ppm a.e. This conservative approach may be the most realistic for triclopyr TEA because it has been determined to lack chronicity. Since triclopyr

TEA appears to lack chronic toxicity even at the very high initial exposure rates, calculations of chronic TWA-EECs are not necessary.

However, since the database is so small, one cannot say that credible risk does not exist for chronic exposure of fish to these products. Also, the EPA has determined that the metabolite TCP must be considered to be persistent in the aquatic environment and has an environmental concentration that may exceed 1% of the LC_{50}. Therefore, an additional freshwater early life-stage toxicity study with rainbow trout or another susceptible salmonid is required. Further research to expand this database on the chronic toxicity of triclopyr TEA and its TCP metabolite to fish needs to be conducted. Typical tests that would be conducted are early life-stage tests with fathead minnow, rainbow trout and sheepshead minnow. A formal risk assessment in Section 4.3.2.5 supports the conclusion of this toxicity review.

- **Chronic effects on Invertebrates**

The amount of data that has been generated on life-cycle effects of triclopyr on aquatic invertebrates is minimal (Tables 2, 10, 19 and 20). A single 21-day life-cycle test has been conducted on triclopyr with *Daphnia magna*.

The life-cycle NOEC, MATC and LOEC for triclopyr are 26, 35 and 48 ppm a.e., respectively for *Daphnia magna*. These values were based on the difference in total young per replicate between daphnids treated with triclopyr TEA and the untreated controls and are well above the maximum expected exposure concentration (EEC) of 2.5 to 4.4 ppm a.e.

Even the highest EECs at the time of application (2.5 to 4.4 ppm a.e.) should not chronically impact *Daphnia magna* since they are well below the chronic MATC concentration of 35 ppm a.e. This conservative approach may be the most realistic for triclopyr TEA because it lacks chronicity. Since triclopyr TEA appears to lack true chronic toxicity even at the very high initial exposure rates, calculations of chronic TWA-EECs are not necessary.

Due to the small size of the database, one cannot say that credible risk does not exist for chronic exposure of invertebrates to triclopyr. Further research on the chronic toxicity of triclopyr to aquatic invertebrates needs to be conducted to give the life-cycle NOECs, MATCs and LOECs greater credibility.

It is worthwhile to conduct a chronic risk assessment assuming that the acute to chronic ratio (10.7) for all invertebrates is the same as that determined for *Daphnia magna*. However, life-cycle tests conducted with species of known sensitivity like *Daphnia magna*, *Ceriodaphnia dubia* and *Mysidopsis bahia* would improve the credibility of this risk analysis. A formal risk assessment in Section 4.3.2.5 supports the conclusion of this toxicity review.

4.3.2.3 Impacts of Single Versus Multiple Applications

It would be extremely rare for lakes in Washington State to be treated with triclopyr products more than once in a season. However, the product has not received an approved label yet and therefore, little opportunity has presented itself for the study of single versus multiple applications of triclopyr TEA.

A one-time treatment of Lake Minnetonka with 2.5 ppm a.e. triclopyr TEA had no significant impact on sentinel (caged) fish. Therefore, triclopyr TEA was not believed to have direct impact on fish survivorship in ponds treated with triclopyr TEA (Petty et al, 1998). Similar results were seen in ponds at Lewisville, TX. However, untreated ponds exhibited similar mortalities (1 and 3% respectively). Therefore, triclopyr TEA was not believed to have a direct affect on fish survivorship in treated ponds.

Limited data from Moses Lake (Washington) with sentinel rainbow trout also indicates that the treatment of wetlands for the control of purple loosestrife did not cause mortalities that significantly exceeded those seen in untreated control areas. There was between 75% and 100% survival of rainbow trout at all treated and untreated control sites. These data indicate that even the sensitive salmonid species should not be adversely impacted in the field when triclopyr is used at appropriate concentrations for the control of purple loosestrife.

Fish collected by either electro-shocking at the Lake Seminole site or as caged sentinel organisms from ponds in Elk Grove, CA, Columbia, MO or Lewisville, TX showed no evidence of mortality. Therefore, it is assumed that no significant mortalities were noted at any of these test sites. It is likely that a wide variety of game and non-game fish will be unaffected by the use of triclopyr at 2.5 ppm a.e. At Lake Seminole, the non-game fish included brown bullhead, common carp, chain pickerel, gizzard shad, lake chubsucker and spotted sucker while the game fish included bluegill sunfish, largemouth bass, redear sunfish, warmouth sunfish and yellow perch. At the pond sites, only bluegill sunfish and catfish were monitored.

Observations on presence of *Rana pipiens* in the field indicates that both adults and tadpoles were common in Columbia, MO test ponds both prior to treatment and through 11-week post-treatment. This data indicates that this ranid frog species was not affected by the use of triclopyr at 2.5 ppm a.e.

Treatments of Moses Lake site for control of purple loosestrife had no significant impact on sentinel (caged) daphnids. The percent survival in both treated and untreated plots was approximately 80%. In situ arthropods collected from activity traps contained greater numbers of branchiopods and copepods at the treated sites than at the untreated sites. However, there were no significant increases or decreases amongst the other most common invertebrate taxa between treated and untreated ponds. Any changes in numbers seen during the experiment were believed to be due to normal seasonal or phenological fluctuations that would typically be seen at the Moses Lake site (Gardner and Grue, 1993).

At the pond sites in Elk Grove, CA, Columbia, MO and Lewisville, TX, the numbers (frequency) of invertebrates increased at the California site, decreased at the Missouri site and shifted in dominant organism at the Texas site due to increases in water temperature. However, the aquatic invertebrate populations were fairly large, healthy and diverse containing both small planktonic forms like water fleas and cladocerans and larger forms like juvenile dragonflies and snails in both treated and untreated ponds (Petty et al, 1998). Since changes were similar across both treated and untreated ponds, it is likely that the fluctuation in invertebrate numbers and dominant organism during the 6- to 12-week evaluation period were caused by normal phenological events.

Additional laboratory work indicates that chronic exposure at high concentrations of triclopyr (mimicking multiple exposures) will probably not cause pathological and biochemical signs of stress in the salmonids (Janz et al, 1991 and Morgan et al, 1991). Experimental data indicate that at concentrations of ~200 ppm Garlon® 3A (72 ppm a.e.), Coho salmon fry will be adversely affected. Fortunately, such high concentrations are clearly not environmentally relevant. However, concentrations that were approximately half the LC_{50} produced threshold changes in the behavior, which included increased ventilatory rates, changes in color as well as a loss of equilibrium and neuromuscular control in rainbow trout. Concentrations of twice the LC_{50} were necessary to produce a significant avoidance response (Morgan et al, 1991). Furthermore, concentrations less than 50% to 80% of the acute LC_{50} had no impact on typical measures of physiological stress in Coho salmon, including no effects on the haematocrit, leucocrit, oxygen consumption, plasma glucose levels and plasma lactate levels (Janz et al, 1991). Although an exposure of 72 to 288 ppm a.e. is clearly higher than would be encountered in the environment, lower concentrations could potentially cause adverse impact on fish. These environmental assaults have the potential to cause additional stress making sensitive species more susceptible to parasites, disease, predators, and other pesticides, as well as impact the ability to feed, avoid predators, find mates and breed. To determine if long-term exposure to environmental concentrations (<2.5 ppm a.e.) is likely to cause subtle adverse impacts would require costly multigenerational studies.

- **Potential impacts on numbers**

  Gardner and Grue (1993) and Petty et al (1998) found that numbers of macro-invertebrates were not impacted by triclopyr TEA treatment rates typically used to control purple loosestrife and Eurasian watermilfoil. These treatments were found to have no adverse impact on the numbers of macro-invertebrates found at Moses Lake, WA and in ponds at Elk Grove, CA or Columbia, MO. Numbers of macro-invertebrates were generally the same at treated sites and at untreated control sites. Any changes in numbers or frequency of macro-invertebrate populations was believed to be due to normal phenological and seasonal changes.

  Numbers of amphibians were observed in a pond at Columbia, MO. The numbers of adult and larval (tadpole) *Rana pipiens* was high prior to treatment at 2.5 ppm a.e. triclopyr TEA and remained high during the 11 weeks of observation at this site.

  Although the numbers of game and non-game fish at Lake Seminole (GA) was not specifically monitored, large numbers of these species were caught by electro-fishing during the course of a study to determine if triclopyr bioaccumulates in edible fish flesh after spot treatment of the Lake Seminole site with 2.5 ppm a.e. Garlon® 3A (Green et al, 1989).

  In activity traps at Moses Lake after treatment for the control of purple loosestrife, the numbers of branchiopods and copepods actually increased after treatment with Garlon® 3A. However, numbers of the other common taxa including ostracods and arachnids did not increase after treatment.

  At pond sites in California and Missouri, the invertebrate communities were relatively diverse and stable during the 6- to12-week assessment period after treatment with triclopyr TEA at 2.5 ppm a.e. The frequency of orders and families as well as the total invertebrate frequency increased at the California site but remained diverse and stable at the Missouri site. The significant species at the Missouri site ranged from small planktonic forms like water fleas and other cladocerans to larger forms like juvenile dragonflies and snails. Although the frequency of macro-invertebrates decreased slightly (~8%) at treated sites in Missouri, this decrease was less than in untreated control ponds (20%). These increases in the frequency of macro-invertebrates was no doubt due to increases in green algae and diatoms during the evaluation period. However, the increases in algal and macro-invertebrate populations did not appear to be due to the direct effects of triclopyr TEA, but to increases in water temperature or slight changes in water quality favored by the species that increased in numbers.

- **Potential impacts on diversity**

  The diversity of fish species caught by electro-fishing in Lake Seminole (GA) was high during the 21 days of evaluation after treatment with triclopyr TEA at 2.5 ppm a.e. The fish population included many species of game and non-game fish. Game fish that were caught included bluegill sunfish, largemouth bass, redear sunfish, warmouth sunfish and yellow perch. Non-game fish that were caught included brown bullhead, common carp, chain pickerel, gizzard shad, lake chubsucker and spotted sucker. The game and non-game fish caught during the six sampling periods in the study did not seem to vary significantly from catch to catch (Green et al, 1989).

  The dominant forms and diversity of invertebrate populations appeared to shift somewhat at the Elk Grove, CA and Lewisville, TX pond sites. However, the diversity in the Columbia, MO ponds treated with triclopyr TEA did not seem to change significantly. At the California site the diversity increased from nine orders and families before treatment to 18 orders and families 12 weeks after treatment. Since this increase in diversity was similar across treated and untreated ponds, it was believed to be due to normal phenological and seasonal events rather than the direct impact of triclopyr TEA.

  In the ponds at Lewisville, TX, there appeared to be a distinct shift in the aquatic community during the 6-week course of the study. Prior to treatment the predominant macro-invertebrates were tadpole shrimp (*Apus*), fairy shrimp (*Eubranchipus*) and water flea (*Daphnia*). By 6-weeks post treatment, the predominant organisms were pond snail (*Physa*), juvenile dragonflies (*Libellulidae*) and phantom midges (*Chaoboridae*). However, since similar shifts in dominant species were seen in both treated and untreated ponds, it appears unlikely that these changes are due the direct impact of triclopyr TEA. Instead, these shifts are believed to be due to warmer water temperatures and other water quality changes that occurred naturally in the post-treatment phase of the study.

- **Potential impacts on habitat use for spawning, rearing and growth**

  - **Effects on Trout and other salmonids**

    Triclopyr has been shown to have low acute toxicity to rainbow trout and salmon and based on the early life-stage study with fathead minnow, triclopyr, probably has a low chronic toxicity to trout and salmon. The commercial formulation of triclopyr TEA has an acute toxicity (96-hour LC_{50}) to trout and salmon that ranges from 82 to 167 ppm a.e. and a predicted chronic toxicity (MATC) that ranges from 27 to 61 ppm a.e. Since triclopyr is not likely to be encountered at concentrations higher than 2.5 ppm a.e. at sites treated for control of submerged weeds or 4.4 ppm at sites treated for control of floating and emergent weeds immediately after treatment, this product is unlikely to cause toxicity in freshwater trout or salmon. Even concentrations as high as 6.6 ppm, which might be encountered after an accidental over-spray with triclopyr TEA to control wetland associated non-aquatic weeds and woody brush, are not likely to cause toxicity to freshwater trout and salmon. Due to triclopyr's very short half-life, salmonids are not likely to be exposed to expected environmental concentrations (EEC) as high as those given above. The typical 4-day TWA-EEC after treatment for control of Eurasian watermilfoil would be 0.85 to 2.1 ppm a.e. (non-time weighted EEC = 0.16 to 1.7 ppm a.e.) assuming a 1- to 7.5-day half-life. Field treatments at 27 to 30 lbs a.e./acre (2.5 ppm a.e.) resulted in observed concentrations in rivers and lakes that varied from <0.05 to 0.47 ppm a.e. 3 days after treatment of the Pend Oreille River, 1.9 to 2.2 ppm a.e. 3 days after treatment at Lake Minnetonka and 1.5 to 2.0 ppm a.e. 3 days after treatment at ponds located in California, Missouri and Texas (Petty et al, 1998; Green et al, 1989 and Getsinger et al, 1997).

Trout fry have been not been noted to avoid triclopyr at concentrations that are environmentally relevant (0.1 to 6.6 ppm a.e.) (Morgan et al, 1991). Furthermore, no avoidance of triclopyr TEA by rainbow trout were seen for trout until the concentration of triclopyr TEA was twice the LC_{50} of 144 ppm a.e. Also, Coho salmon only exhibited threshold behavioral changes involving increased ventilatory rates, changes in color, erratic swimming and loss of neuromuscular control at concentrations of triclopyr that approached the LC_{50} (e.g. 72 to 115 ppm a.e.). Although field studies conducted to observe acute toxic effects and bioconcentration were conducted at Lake Minnetonka, Lake Seminole and ponds in California, Missouri and Texas, no comment was made on observed behavioral effect involving fish at these sites. However, the environmental relevance of this observation is not entirely clear since the concentrations that cause laboratory effects are much higher than would be typically encountered in the environment. Therefore, avoidance of triclopyr exposure is probably not possible in real field treatment situations. However, it is noteworthy that fish driven from habitat by avoidance behavior, may not be able to obtain necessary resources for survival in other habitats. These resources could include, food, refuge, mates and appropriate egg-laying (substrate).

The greatest concern may be managing aquatic plants so that maximum breeding opportunities can occur. It typically takes concentrations of 0.75 to 2.5 ppm a.e. triclopyr TEA to effectively manage aquatic foliage. However, exposure (starting in June of any given year) to ~0.25 ppm a.e. will control Eurasian watermilfoil. Various treatment rates have been found to be effective in controlling Eurasian watermilfoil and control has been achieved in the laboratory and in mesocosm studies at concentrations of 0.25 to 2.5 ppm a.e. The degree of control achieved depended on treatment rate and exposure time. Native plant species including *Ceratophyllum desmersum*, *Elodea canadensis, Heteranthera dubia*, and various pondweed species thrived after the elimination of Eurasian water milfoil from treatment sites in the Pend Oreille River (WA) (Getsinger et al, 1997 and Netherland and Getsinger, 1993). The consequences of eliminating Eurasian watermilfoil from a habitat and replacing it with native species can have tremendous impact. Replacement of noxious weed species with a more diverse native aquatic plant community may result in improvements to the environment that attract fish and wildlife to an area where these animals were not numerous prior to treatment (Frank, 1972). Due to the effects of erosion by floods, the character of a habitat may be changed from one suitable for the reproduction of sunfish to one suitable for the reproduction of salmonids.

- **Effects on salmon smoltification**

Evidence for effects on salmon smoltification from the use of triclopyr is not currently available. There have been no seawater challenges conducted with salmon parr-smolt after exposure to sublethal concentrations of triclopyr TEA. However, exposure of Coho salmon to high concentrations of Garlon® 3A found no statistically significant effect on plasma glucose, haematocrit or leucocrit at concentrations up to (72 to 115 ppm a.e.), which is approximately 50% to 80% of the 96-hour LC_{50}. The only physiological parameter that was higher than the controls was the plasma lactate level. However, even this parameter was unaffected by exposure to concentration triclopyr TEA that was less than 200 ppm formulation equivalence (72 ppm a.e.). Although oxygen consumption was elevated over the controls at these concentrations, it was not statistically different from the controls. A number of herbicides have been noted that effect the seawater survivability or behavior of salmon after they have been exposed to herbicide concentrations similar to the expected environmental concentration. For example, Aquathol® and Hydrothol® 191 have been observed not to be acutely toxic to Chinook salmon at 3.0 ppm a.e. and 0.2 ppm a.e., respectively. However, after exposure to these concentrations of endothall products, approximately 100% and 45% of the smolts, respectively did not survive (Bouck and Johnson, 1979 in Shearer and Halter, 1980 and Serdar et al, 1995). Fifteen to eighty seven percent of Coho salmon exposed to 5 to 20 ppm a.e. diquat did not survive a subsequent seawater challenge; and although subsequent tests indicated that Coho salmon smolts could survive a seawater challenge after exposure of up to 3.0 ppm a.e., these fish were adversely impacted in their ability to migrate down stream after exposure to 0.5 to 3.0 ppm c.e. diquat. Treatment of Coho salmon with Amitrol®-T, diquat and paraquat caused dosage related mortality in subsequent seawater challenge tests. However, concentrations as high as 50 ppm for Amitrole® –T, 1.0 ppm for paraquat and 5 ppm c.e for diquat were necessary before significant mortality occurred in seawater challenge tests (Lorz et al, 1979). Copper chloride (cupric copper) is very highly toxic to Coho salmon with and acute LC_{50} of 0.06 to 0.074 ppm copper. The effects of copper chloride in a seawater challenge test showed an even higher toxicity with a 6% to ~100% mortality occurring after exposure to 0.005 to 0.03 ppm copper. Furthermore, the higher concentrations of copper chloride also caused a depression in the activity of NA^+/K^+ ATPase by as much as 75%. Exposure to copper chloride concentrations as low as 0.005 ppm copper cause a reduction in and a 20% decrease in down stream migration (Lorz and McPherson, 1976). Higher concentrations of these herbicides may cause histopathological effects in a number of species of salmon and trout. Sub-lethal freshwater concentrations of the herbicides 2,4-D BEE and 2,4-D DMA do not cause subsequent salmon mortality in saltwater challenges. Mortalities in subsequent seawater challenges and changes in Na^+/K^+ ATPase levels were not seen after exposure of Coho salmon to 200 ppm a.e. 2,4-D DMA (Lorz et al, 1979). Furthermore, low concentrations of 2,4-D BEE (1.0 ppm) and short exposure periods (24 hours) had no effect on subsequent seawater challenge survival in Coho, sockeye or pink salmon (Martens, 1979 in Shearer and Halter, 1980). However, exposure of these species in freshwater for 96 hours to 1.0 ppm 2,4-D BEE kills all of these test fish. Of all these compounds, triclopyr TEA is most closely related to 2,4-D DMA. Since we know that both triclopyr TEA and 2,4-D DMA are only slightly to practically nontoxic to salmon species, it seems unlikely that triclopyr TEA will cause adverse impact when salmon smolts are challenged by seawater subsequent to a freshwater exposure.

These results indicate triclopyr products used for control of aquatic weeds are unlikely to impact the smoltification process. However, this is an untested hypothesis and should be considered with caution until empirical evidence is available.

There have been no reports of relatively high concentrations of triclopyr (72 to 115 ppm c.e.) causing significant physiological or histopathological effects on salmonids or other fish. In fact, no sub-acute impact has been noted on the tested fish species other than a doubling in the plasma lactate concentrations, which is often considered a sign of acute stress. At concentrations as high as 40 ppm formulation equivalence (14 ppm a.e.), there are no observed physiological, histopathological or behavior effects. Since the concentration of triclopyr used to control submerged weeds is only 2.5 ppm a.e. and the concentration of triclopyr used to control emerged weeds would not be higher than 4.4 ppm a.e. (6.0 Kg a.e./ha), it seems unlikely that significant sub-acute effects would occur in the field (Morgan et al 1991 and Janz et al, 1991). However, it is unclear if sub-acute triclopyr concentrations typically found in the field could have subtle behavioral effects on the resident fish population. These subtle effects could impact feeding, predator avoidance, resistance to parasites and disease, finding mates, mating and breeding.

- **Effects on sea-run cutthroat trout and sea-run steelhead trout**

No work was found on the effect of triclopyr on sea-run cutthroat trout or steelhead. General acute toxicity data has been observed only on salmon and trout species. These effects have been described under effects on trout and other salmonids and effects on salmon smoltification. It seems likely that cutthroat trout and sea-run steelhead trout would respond in a manner similar to salmon. Other andromonous species of concern could include the American eel (*Anguilla rostra*), and the striped bass (*Morone saxatilis*). However, acute data on these species is not available.

A potential complicating factor with sea-run cutthroat trout (*Oncorhynchus clarki*), and steelhead trout (*Oncorhynchus mykiss*) is similar to the parr to smolt metamorphosis except that these sea-run trout may go through this process several times in their lifetime including each time the adults migrate to the sea and the initial parr to smolt metamorphosis. However, seawater challenge, feeding inhibition tests, predator avoidance test or migration inhibition tests have not been conducted with any of these andromonous species.

- **Effects on other species (sunfish, minnow and catfish)**

The acute and chronic toxicity of triclopyr are very low in fish. The acute LC_{50}s for the current formulation range from 86 to 176 ppm a.e. for the tested species [bluegill sunfish (*Lepomis macrochirus*) and flathead minnow (*Pimephales promelas*)]. The only stage that was tested for acute toxicity in the laboratory were fry around 16 to 31 mm in length (Table 17). For Fathead minnow, the chronic 31-day LC_{50} (52 to 81 ppm a.e.) was similar to the acute flow-through toxicity [(96-hour) LC_{50} = 86 ppm a.e.)] (Tables 17 and 19). This leads to the conclusion that the chronicity of triclopyr TEA is low for fish and the short-term and long-term LC_{50}s will be similar for all exposure periods longer than 24 hours. The long-term LOEC and LC_{50} are not significantly different from each other and the long-term NOEC due to the experimental design is only about 2-fold less than the long-term LOEC.

It is noteworthy that changes in water hardness can strongly affect the toxicity of some herbicides. For example, 2,4-D, diquat and endothall, are all affected by hardness to a certain degree. For example, the LC_{50} of Hydrothol® 191 is much lower in hard water (0.32 to 0.96 ppm) than in soft water to (1.18 to 1.6 ppm); the LC_{50} of 2,4-D 2-EHE is lower in hard water (21 to 79 ppm) than in soft water (30 to 167 ppm); the LC50 of diquat is lower in soft water (7.6 to 39 ppm c.e.) than in hard water 76 to 125 ppm c.e.). Based on the pKa, (2.68), it is unlikely that pH or hardness will have significant impact on the toxicity of triclopyr TEA at levels typically found in natural water (pH 5.0 to 9.0). Water hardness did not significantly impact the fish toxicity of 2,4-D diethanolamine: the LC_{50} of 2,4-D diethanolamine in soft water ranged from 291 to 472 ppm while the LC_{50} in hard water ranged from 438 to 662 ppm. Therefore, it seems unlikely that hardness will significantly impact the toxicity of this 2,4-D product at concentrations likely to be found in the field (<4.8 ppm). Since triclopyr TEA (an analog of 2,4-D diethanolamine) has a similar range of toxicity, it also seems unlikely that its toxicity will be significantly impacted by water hardness or pH when fish are exposed to maximal environmental concentrations (2.5 to 4.4 ppm c.e.).

The chronic MATCs for triclopyr on *Pimepahles promelas* is equal to 41 ppm a.e. The estimated chronic MATC for all fish species tested for acute toxicity ranges from 27 to 61 ppm based on the acute to chronic toxicity ratio of 3.0. Since the initial application rate (worst case EEC of 2.5 to 6.6 ppm a.e.) is much less than the predicted chronic MATC, it is unlikely that these typical long-term EECs of triclopyr will adversely affect sunfish, or minnow biota. Laboratory studies have not been conducted with catfish. However, work done in the field with sentinel (caged) catfish and other fish species indicates that toxicity in the field is unlikely to be a serious issue when triclopyr TEA is used to control aquatic macrophytes. For example, a one-time treatment of Lake Minnetonka with 2.5 ppm a.e. triclopyr TEA had no significant impact on sentinel (caged) fish. Although low oxygen concentration was seen to cause mortality in 26% of the suckers, 11% of the largemouth bass and 5% of the bluegills, similar effects were seen in untreated control ponds. Therefore, triclopyr TEA was not believed to have direct impact on survivorship in treated ponds (Petty et al, 1998). Similar effects were seen in ponds at Lewisville, TX where sunfish had a mortality of 1% and catfish suffered a 10% mortality in treated ponds. However, untreated ponds exhibited similar mortalities (1% and 3%, respectively).

Therefore, triclopyr TEA was not believed to have a direct affect on fish survivorship in treated ponds.

The effects of triclopyr on behavior and metabolic responses in wild fish are a potential concern. A discussion of these behavioral effects is included in the sections entitled “Effects on Trout and Other Salmonids and Effects on Salmon Smoltification”. The rainbow trout and salmon were only impacted in behavior and metabolic response at concentrations much higher than typical expected environmental concentrations (2.5 to 4.4 ppm a.e.). Concentrations that caused changes in behavior including avoidance, erratic swimming and labored respiration range from 72 to 288 ppm a.e., which is near the acute LC_{50} for rainbow trout and salmon. Concentrations that produce metabolic effects on salmon were >72 ppm a.e. which is about half the LC_{50} for salmonids (Morgan et al, 1991 and Janz et al, 1991.

It is apparent that the size structure and the forage fish to game fish (predator) ratio is impacted significantly to the amount of plant cover and filamentous algae present. However, the plant cover areas that allow for the best size structure and F/P ratio vary considerably between water bodies (Swingle, 1956 and Swingle 1950). Creation of more open water with fewer macrophytes may increase fish habitat. Alternatively, some juvenile fish use milfoil communities as a refuge area from predators and as general habitat. Small fish looking for refuge probably use the edge and not the entire milfoil stand.

Feeding behavior of fish may also be affected in water bodies treated with aquatic herbicides. For example, grass carp have been observed to not eat at diquat concentrations that were only one-fifth of the LC_{50}. The author (Tooby et al, 1980) contended that it was reasonable to expect that these fish would also exhibit reduced feeding rates at concentrations typically seen in the environment. Although similar experiments were not performed with triclopyr, it seems unlikely that fish would be affected by concentrations of triclopyr TEA found in the environment since general behavior, physiology and biochemistry were not affected by concentrations of triclopyr that approached the LC_{50} for rainbow trout and salmon.

- **Effects on invertebrates**

Data on the field effects of triclopyr on aquatic invertebrates is fairly extensive. However, it has been observed that although the population number and diversity of macro-invertebrates could vary extensively after treatment with triclopyr TEA at 2.5 ppm, similar effects were seen in the control. These variations in macro-invertebrate numbers and diversity were believed to be due to normal phenological events associated with the change in season. These phenomena were previously discussed in the section entitled “Potential Impacts on Numbers and Potential Impacts on Diversity”. With the possible exception of the eastern oyster, the acute and predicted chronic exposures to triclopyr TEA are significantly less than the EEC. With the eastern oyster, the acute LC_{50} is less than ten-fold higher than the EEC or TWA-EEC and therefore a potential acute impact on these bivalves is remotely possible. Since the LC_{50} > two-fold higher than the EEC or TWA-EEC, triclopyr as a restricted use formulation will probably prevent adverse impact on these bivalves. However, since the predicted chronic MATC on these bivalves is fairly low (MATC = 2.1 to 3.8 ppm a.e.) and may not exceed the EEC (2.5 to 6.6 ppm a.e.) and TWA-EEC (1.1 to 2.9 ppm a.e.), triclopyr used at typical maximum use rates may adversely impact reproduction and growth of the eastern oyster. Since the use of triclopyr TEA is not permitted in estuaries and any triclopyr transported to an estuary is likely to be highly diluted by both advection and dispersion from freshwater with further dilution by marine tide water, it seems unlikely that the concentrations of triclopyr in estuarine water would be high enough to adversely impact the eastern oyster or other estuarine species.

Freshwater species that were tested are also not likely to be affected by treatment with triclopyr TEA to control aquatic weeds since the LC_{50} for these species ranges from >103 to 376 ppm a.e. in red swamp crayfish and *Daphnia magna*. The measured or predicted MATCs for these species were >9.6 and 35 ppm a.e., respectively. These toxicity values are 5- to 10-fold higher than the EEC, which makes adverse impact on freshwater invertebrates unlikely.

The safety factor for these aquatic invertebrates can be improved if the dosage of triclopyr TEA is decreased. Although the maximum use rate for the control of submerged aquatic weeds has been reported to be 2.5 ppm a.e., lower concentrations have been observed to effectively control Eurasian watermilfoil.

In laboratory and mesocosm studies, triclopyr has been observed to control Eurasian watermilfoil at concentrations that range from 0.25 to 2.5 ppm a.e. In the field, 1.0 ppm a.e. triclopyr TEA was only slightly less effective than 2.5 ppm a.e. in controlling Eurasian watermilfoil at Lake Seminole. However, in the Lake Seminole case, neither treatment rate was totally effective in controlling Eurasian watermilfoil due to extremely rapid dissipation (dispersion and advection). Furthermore, 1.75 ppm a.e. was effective in controlling Eurasian watermilfoil in coves of the Pend Oreille River. The lowest effective concentration of triclopyr TEA should be used to control Eurasian watermilfoil so that native species like coontail, American waterweed and various pondweed species are likely to flourish (Netherland and Getsinger, 1993; Getsinger et al, 1997 and Getsinger and Westerdahl, 1984).

- **Interaction of water quality with Triclopyr products and their commercial recommended adjuvants**

Water quality encompasses many parameters, but the toxicity of chemicals to fish is most often influenced by water hardness, pH and the inter-related factors of temperature and dissolved oxygen.

None of the water quality parameters were investigated in relationship to triclopyr TEA toxicity. In the field studies conducted with triclopyr, water quality was not observed to be adversely impacted by treatment with triclopyr. Generally speaking, hardness, pH, turbidity, dissolved oxygen content and conductivity can influence water quality. After treatment with triclopyr TEA, water quality changes as a result of diel effects and seasonal changes have been seen. However, water quality changes have not been observed in treated lakes and ponds that did not also occur in control lakes and ponds.

Dissolved oxygen content was generally observed to be high during daylight hours and low during nighttime hours. Although some fish-kill (5% to 26%) in Lake Minnetonka were attributed to asphyxiation after treatment with triclopyr, similar fish-kills were seen in control ponds. Suckers, largemouth bass and bluegill were adversely impacted by low DOCs. However, brown bullhead, crayfish and clams were not affected in ponds where low DOC values were found (Petty et al, 1998).

It is likely that nutrient levels along with moderate/stable spring and summer water temperatures resulted in the increase of several genera of green algae at Lake Minnetonka, Lake Seminole and ponds in California, Missouri and Texas (Petty, et al, 1998; Foster et al, 1997; Foster et al, 1998; Houtman et al, 1998 and Green et al, 1989). At the same time, blue-green algae decreased at treated sites but not at control sites. The increase of green algae like *Spirogyra*, *Mougeotia*, *Volvox*, *Closterium* and *Scenedesmus* have the potential to improve the nutrition of planktovoric fish and invertebrates. However, no changes in fish or invertebrate population size or diversity could be absolutely correlated with increase in the numbers of these algae species. Increases in the invertebrate population size and diversity may have been affected by a variety of water quality and biological factors that could not be attributed to the effects of triclopyr TEA treatments. These factors changed as a result of normal phenological changes that occur as the seasons progress.

No work has proven conclusively that triclopyr TEA has antagonistic, better than additive effects, cumulative effects or synergistic effects when combined with other herbicides. However, certain trends have been observed and they are discussed extensively in Section 4.2.4. E.g., there is some evidence that triclopyr combined with a surfactant (Kinetic®) at concentrations of 0.125% w/w improved the activity of triclopyr TEA against *Eichhornia crassipes* (Langeland and Smith, 1983). Additive effects have also been seen when triclopyr TEA is combined with diquat for the control of waterhyacinth and water lettuce. Since triclopyr has been determined to exhibit little or no chronicity, it is unlikely that it has cumulative effects (Gersitch et al, 1984: Wan et al, 1987: Mayes et al, 1984 and Batchelder, 1973). No specific studies indicate that triclopyr TEA is antagonistic with other pesticides. However, ionic-surfactants must be avoided since they may react with or be antagonistic to the action of triclopyr.

In the State of Washington, triclopyr products are rarely mixed with other products. However, for the control of floating or emergent plant species, the use of nonionic surfactants is highly recommended (Renovate® and Garlon® 3A labels). Also the use of thickening agents or invert-emulsions is recommended for applications of triclopyr to control submerged aquatic macrophytes. A number of surfactants are registered for use with water-soluble herbicides like triclopyr but expert advice should be sought to avoid using ionic surfactants or those that may be otherwise incompatible with triclopyr. Professional researcher (Kurt Getsinger) believes that when triclopyr is applied to floating or emergent vegetation that a nonionic surfactant and/or drift control agent should be used. Furthermore, a thickener or invert-emulsion is often used with liquid products applied by subsurface injection to allow the treatment to sink more deeply into the water column where it can be most effective.

There are a number of adjuvants registered for aquatic use in Washington State. Most nonionic surfactants should be mixed at 0.25% to 0.5% by weight of application solution when triclopyr is being applied to floating (surface) or emergent aquatic macrophytes. The toxicity of these adjuvants to bluegill sunfish, rainbow trout and daphnia has been well documented. None of these aquatic adjuvants should be toxic to fish or aquatic invertebrates when applied at labeled rates. However, it has been noted by Watkins et al (1985) that some aquatic adjuvants have a potential to be toxic to aquatic organisms when applied in shallow water. For example: 1) If Spar-Mate® is applied at the labeled use rates to water with a depth of less than 1.5 meters, it can be toxic to bluegill sunfish; 2) If Cide-Kick®, X-77®, Formula 403®, or IVOD® are applied at the labeled use rate to water with a depth of less than 0.1 meters, they may be toxic to fish. Since the depths given are for concentrations of the adjuvant that will kill 50% of the treated animals, an additional safety factor of ~10-fold would need to be added to assure safety of the adjuvant to the biota. Details of the toxicity and depth considerations for a number of aquatically applied adjuvants can be found in Table 8. Although adjuvants are typically considered to be “nearly inert”, they are not entirely inert. Adjuvants can enhance, diminish, or have no effect on the activity of herbicides. Although acute aquatic testing has been done on a number of adjuvants, insufficient data exists to appropriately evaluate risk from the toxic effects of adjuvants when mixed with herbicides and applied to the aquatic ecosystem.

All formulations of triclopyr may not be similar in toxicity on an acid equivalence (a.e.) basis. We know that commercial triclopyr formulations may have radically different toxicity to fish and invertebrates. For example, the toxicity of triclopyr TEA (Renovate® and Garlon® 3A) with LC_{50}s of 240 to 1,170 ppm formulation equivalence is approximately 100-fold less toxic than triclopyr BEE (Garlon® 4) with LC_{50}s of 0.65 to12 (EPA RED, 1998). However, only triclopyr TEA products are labeled for use in public waterways. Those formulations, which are not labeled for use in public waterways, should not be used in public waterways. If new formulations are registered for use in public waterways, caution should be practiced since all inert materials are not equivalent. The “inert materials” and contaminants may interact with the pesticide to give antagonistic, additive, cumulative or synergistic effects against target aquatic plants and algae, and non-target fish and aquatic invertebrates.

4.3.2.4 Effects on Endangered Species

There are a number of species that have been classified as sensitive, endangered or threatened. These include several species of salmon, 13 species of rockfish, 2 species of herring, 2 species of dace, and 8 species of amphibians. A list of these species can be found in Appendix 1. However, the salmonid species are not acutely affected by triclopyr at concentrations that will typically be found in the environment. For example, *Oncorhynchus* salmon species have LC_{50} values that range from 96 to 167 ppm a.e. and these values are in great excess of the most typical initial EEC (2.5 to 6.6 ppm a.e.) or the 4-day TWA-EEC (2.1 to 5.5 ppm c.e.). Therefore, these species are unlikely to be acutely impacted by typical field rates of triclopyr. There is no evidence that triclopyr TEA will impact salmon smoltification. However, since there are no studies examining the effects of triclopyr TEA on the smoltification of salmon, care should be used when using triclopyr to avoid application of this product when salmon are smolting, spawning or migrating.

1.3

4.3.2.5 Risk Analysis for Aquatic Species

Summary: Based on the acute toxicity determined in the laboratory, triclopyr is unlikely to adversely impact the fish biota. However, the invertebrate biota, particularly, estuarine bivalves, may be adversely impacted since the most sensitive species of bivalve (eastern oyster) has a demonstrated LC_{50} (22 to 41 ppm c.e.) that is in the same order of magnitude as the EEC or short-term TWA-EEC. The most sensitive species of bivalve will probably not be affected by applications of 2.5 ppm a.e. to control submerged aquatic macrophytes. However, applications of 4.4 ppm c.e. (6.0 lbs a.e./acre) to control emerged aquatic macrophytes or applications at 6.6 ppm a.e. (9.0 lbs a.e./acre) to control woody brush and terrestrial broadleaves in riparian areas may adversely impact these species and species with similar sensitivities. Nevertheless, all other species of aquatic invertebrate and fish should not be adversely impacted since the LC_{50} (>103 to 376 ppm a.e.) is more than10-fold higher than the aforementioned EEC or short-term TWA-EEC. Available field data supports the conclusion that was reached with laboratory data. No direct or secondary effects of triclopyr TEA have been observed for fish and aquatic invertebrates. Secondary effects may impact the aquatic biota in either a positive of negative manner. Reduced dissolved oxygen content may cause death of fish by asphyxiation, but no difference between treated and control sites was noted. Increases in nutrient levels can lead to an increase in the number of phytoplankton and a potential improvement in the condition of species that feed on phytoplankton. Short-term decreases in the number of phytoplankton present have also been observed. This decrease in the phytoplankton count can potentially lead to decreases in biomass (yield) of planktovoric amphibians and fish.

A great deal of data relevant to the risk analysis was discussed in Sections 4.2.3.2.1 Acute Effects and 4.2.3.2.2 Chronic effects. However, no formal risk analysis was actually performed in those sections.

Certain mitigating behavioral and toxicity factors can improve the Risk Assessment picture. However, fish have not been observed to avoid triclopyr TEA until the concentration exceeds the LC_{50} (144 ppm a.e.) for rainbow trout. Furthermore, other behavioral and physiological effects have not been observed in rainbow trout or Coho salmon until the concentration of triclopyr TEA is 50% to 80% of the LC_{50} (Morgan et al, 1991 and Janz et al, 1991).

Typical concentrations of triclopyr can be predicted from EPA's worst case scenario application of 2.5, 4.4 or 6.6 ppm a.e. and a half-life of 7.5 days for the control of submerged, emerged and riparian weeds. These 4-day TWA-EECs would average around 2.1, 3.7 and 5.5 ppm a.e., respectively during the 4 days of acute exposure. Modeling work for potable water systems does not apply directly to the aquatic risk assessment of triclopyr. Details of the models conclusions can be found in Section 4.2.3.2. Since exposure to diquat appears to have its maximum effect within 24 hours, the use of a TWA-EEC may be unwise. Although TWA-EECs have been calculated, the initial EEC may be more demonstrative of risk to aquatic organisms even in cases where chronic risk is being evaluated.

Since these results are fairly consistent, the expected environmental concentrations (EEC) for triclopyr TEA have been estimated to be 2.5 to 6.6 ppm a.e. for both acute and chronic effects. If TWA-EEC values are considered necessary, the 2-day TWA-EEC ranges from 2.3 to 6.0. ppm a.e.; the 4-day TWA-EEC ranges from 2.1 to 5.5 ppm a.e.; the 21-day TWA-EEC ranges from 1.1 to 2.9 ppm a.e.; the 28-day TWA-EEC ranges 0.89 to 2.4 ppm a.e.; and the 31-day TWA-EEC ranges from 0.82 to 2.2 ppm a.e. However, since the dissipation of triclopyr is so rapid (<1 day to 7.5 days), another legitimate approach is to assume that no chronic exposure is possible and all aquatic animals will be protected from the chronic effects of triclopyr.

Due to non-linear dissipation, the dissipation rate of triclopyr in the field is difficult to determine. Therefore, the EECs used in these risk assessments are based on linear dissipation models of expected environmental concentrations for short periods (2 and 4 days) and for longer periods (21, 28 and 31days). These time frames correspond to ones that are considered to be acute and chronic exposures, respectively. However, field data indicate that concentrations found in the field are similar to those generated by the predictive models. For details of concentrations found in the field, see Sections 4.2.2, 4.2.2.1, 4.2.2.2, 4.2.2.3 and 4.2.2.4.

- **Acute risk assessment**

  In general, risk assessment for protection of the biota takes into consideration two factors:

  1) The typical environmental concentrations of the pesticide that the biota will be exposed to for short periods of time (1 to 4 days).

     Due to the lack of chronicity, time-weighted average EECs may not be appropriate for Triclopyr. The EECs found immediately after application are 2.5, 4.4. and 6.6 ppm a.e. for control of submerged weeds, emerged weeds and wetland weeds. In the case of wetland weeds, it seems unlikely that the concentration in the water body would ever be as high as 6.6 ppm a.e. unless an accidental over-spray of 9 lbs a.e./acre occurs to a water body that is only six inches deep. Nevertheless, the 2-day TWA-EEC ranges from 2.3 to 6.0 ppm a.e. and the 4-day TWA-EEC ranges from 2.1 to 5.5 ppm a.e. These time-weighted EEC values assume an initial worst case concentration of 2.5 to 6.6 ppm a.e. and a half-life of 7.5 days. This was the longest half-life obtained in several studies and half-lives range from <1.0 days to 7.5 days. Due to this wide variance, it was not possible to determine a typical half-life. Therefore, the longest half-life of 7.5 days was used to model the worst case scenario.

The work of Petty et al (1998) as described in Table 5 gives the daily concentrations detected after application of 2.5 ppm a.e. These values for the California pond were 2.29, 2.08, 2.08, 2.02 and 1.70 ppm a.e. at 0-, 1-, 2-, 3- and 5- days, respectively. Other data is also given for situations where the water dissipation half-life is about 6 days. However, the predicted values based on this 2.5 ppm a.e. treatment rate are reasonably close to the values given above and the calculated EECs for any given day are 2.5, 2.3, 2.1, 1.9, and 1.57 ppm a.e., respectively, which is in good agreement with experimental results.

2) The 96-hour toxicity (LC_{50}) of the pesticide to the most sensitive environmentally relevant species is as follows:

For triclopyr TEA (Renovate® or Garlon® 3A), the most sensitive environmentally relevant fish size class and species are rainbow trout fry (53 mm, 1.1 g) with a 96-hour LC50s of 82 ppm a.e. Other species of fish with similar sensitivity to triclopyr TEA include 0.10 gram fry of tidewater silverside (*Menidia beryllina*) (96-hour LC_{50} = 93 ppm a.e.), chum salmon fry (*Oncorhynchus keta*) (96-hour LC_{50} = 96 ppm a.e.) Chinook salmon fry (*Oncorhynchus tshawytscha*) (96-hour LC_{50} = 99 ppm a.e.) and fathead minnow fry (96-hour LC_{50} = 86 ppm a.e.). Typically, other exposure time frames (24 hours or longer) produce similar LC_{50}s so the initial concentration of 2.5 to 6.6 ppm a.e. should probably be used as the EEC. As these proposed EECs are so much lower than the LC_{50}s, it is not necessary to perform a risk assessment for fish beyond this most conservative approach.

The most sensitive size class and species of aquatic invertebrates is the bivalve eastern oyster (larvae/embryo and spats) with a 48- to 96-hour LC_{50}s of 22 to 41 ppm a.e. All other species were much less sensitive to triclopyr TEA with 48- to 96-hour LC_{50}s that range from >103 ppm a.e. for the red swamp crayfish to 376 ppm a.e. for *Daphnia magna*. Insufficient data exits for positive proof, but exposure time frames beyond 24 hours are likely to yield similar LC_{50}s with the invertebrate species tested. Other species of invertebrate with similar sensitivity to triclopyr TEA include 1st instar *Daphnia pulex* (48 hour LC_{50} = 360 to 367 ppm a.e.), 1st instar grass shrimp, (96-hour LC_{50} = 234 ppm a.e.) and 1st instar pink shrimp (96-hour LC_{50} = 281 ppm a.e.).

- **Acute risk assessment with Triclopyr**

Triclopyr does not have significant toxicity to the most sensitive fish species tested (Table 20). The risk quotient for the most sensitive fish species tested is below the level of concern (0.1) for protecting the biota (RQ = EEC/LC_{50} = 6.6 ppm a.e./82 ppm a.e. = 0.080). Therefore, this segment of the biota is not likely to be adversely impacted by exposure to triclopyr TEA at concentrations typically used to control submerged weeds (2.5 ppm), emerged weeds (4.4. ppm a.e.) or weeds found in wetland situations (6.6 ppm a.e.) where accidental over-sprays of shallow water bodies may occur.

However, higher treatment rates may adversely impact endangered species. Since the level of concern for endangered species is only 0.05, salmon species may be at risk, but only at the highest potential use rate. For example: at an EEC of 2.5 ppm a.e., the risk quotient for the salmon species tested is 0.013 to 0.03; and at an EEC of 4.4 ppm a.e. (6.0 lbs a.e./acre), the risk quotient for salmon species is 0.027 to 0.044. These values are clearly low enough so that is unlikely that these endangered members of the fish biota would be at risk. Nevertheless, in wetland triclopyr TEA treatments of 9.9 lbs a.e./acre (6.6 ppm a.e.), the endangered species acute risk quotient slightly exceeds the level of concern for the most sensitive salmonid species (RQ = 0.036 to 0.066). Therefore, while the endangered salmon biota would not be affected by treatments for control of submerged (2.5 ppm) and emerged (4.4 ppm a.e.) aquatic weeds, treatment for the control of other wetland weeds (6.6 ppm a.e.) could adversely impact the more sensitive salmonids. This is only likely to occur if an accidental direct over-spray to shallow water (6 inches deep) occurred. However, if care is taken, direct over-sprays should not occur and endangered salmon species should not be adversely impacted.

In US EPA evaluation of pesticides under FIFRA, an acute Risk Quotient of higher than 0.1 is interpreted as exceeding the Level of Concern, and leads to the conclusion that the risk may be unacceptable unless further analysis shows otherwise (Urban and Cook, 1985). The general practice in risk assessment is to estimate the Expected Environmental Concentration (EEC) based on the highest expected initial concentration and the most representative half-life. Therefore, triclopyr should be safe to fish when used at or below the maximum use rate under all registered treatment scenarios. Renovate® and Garlon® 3A are registered for control of woody plants and broad leaf weeds in forests, terrestrial non crop sites, such as industrial sites, right of-way, fence rows, non-irrigation ditch banks and around farm buildings, including application to grazed areas and establishment and maintenance of wildlife openings within these sites; and in aquatic sites such as ponds, lakes, reservoirs, marshes, and wetlands including banks and shores within or adjacent to these sites.

The more sensitive species of invertebrates in the biota may be at risk. Environmental exposure of the most sensitive species of aquatic invertebrates may adversely impact bivalves. However, using the more liberal ECOFRAM approaches to risk assessment, it seems unlikely that these species would be acutely affected by triclopyr since the LC_{50}s for the eastern oyster (22 to 41 ppm a.e.) are at least 3- to 9-fold higher than the initial EEC values. Although the risk quotient generated from these EEC and LC50 values for eastern oyster is higher than the low level of concern (0.1) (RQ = 0.11 to 0.3), it is lower than the high level of (0.5). Therefore, if triclopyr is used as a restricted use formulation, it appears unlikely that adverse impact to bivalves or other aquatic invertebrates would occur. Since all other acute LC_{50}s (>103 to 376 ppm a.e.) for aquatic invertebrates (arthropods) are more than 10-fold higher than the initial EEC, other species of freshwater and estuarine invertebrate are unlikely to be adversely impacted by the aquatic use of triclopyr at concentrations of 2.5 to 6.6 ppm a.e.

Field data in Lake Minnetonka indicates that caged (sentinel) suckers, sunfish, brown bullhead, catfish, fresh water clams and crayfish are not affected by exposure to triclopyr TEA at concentrations of 2.5 ppm a.e. More sensitive species may be impacted by asphyxiation if an oxygen slump occurs. However, in the evaluated studies, oxygen slumps occurred in both treated and untreated areas of Lake

Minnetonka (Petty et al, 1998). Furthermore, other work in Lake Seminole indicates that a wide variety of non-game and game fish are also unlikely to be adversely impacted by treatment with triclopyr TEA at concentrations as high as 2.5 ppm a.e. (Green et al, 1989). These species include non-game species like brown bullhead, common carp, chain pickerel gizzard shad, lake chubsucker and spotted sucker, while game fish species include bluegill sunfish, largemouth bass, redear sunfish, warmouth sunfish and yellow perch.

Field Studies at Moses Lake indicate that control of purple loosestrife with triclopyr at up to 3-times the recommended use rate had no adverse impact on caged sentinel rainbow trout or *Daphnia magna*. The most frequently collected taxa in activity traps and in sediment cores were not adversely impacted by the effects of triclopyr TEA applied at Moses Lake. In fact, branchiopods and copepods significantly increased in numbers 7 days after treatment. Similar increases in branchiopod and copepod numbers were not seen in control plots. Other common species of invertebrate like ostracods and arachnids did not increase or decrease in numbers after treatment with triclopyr TEA. The most frequently collected taxa in sediment core samples included amphipoda, diptera, and odonata; in these most common sediment taxa, there were no significant changes in the numbers at one and seven days post-treatment in either the control or treated plots. Other taxa collected in sediment cores included nematoda, gastropoda, ephemeroptera and oligochaeta but their numbers were insufficient to determine if they were affected by exposure to triclopyr TEA. Tank mixes of 6% formulation equivalence resulted in water concentrations as high as 0.883 ppm triclopyr. This concentration is much less than the concentrations determined in our risk assessment to impact invertebrate populations or fish. Furthermore, Gersich et al (1984) has determined independently that the maximum acceptable environmental concentration of Garlon® 3 is 110 ppm formulation equivalence (~40 ppm a.e.). However, it is unlikely that Gersich et al considered the results of the more sensitive bivalve species like the eastern oyster.

Extensive monitoring of various invertebrate species in ponds treated with triclopyr at 2.5 ppm a.e. indicates that this concentration had no direct adverse impact on aquatic invertebrate species found in ponds located in Elk Grove, CA, Columbia, MO or Lewisville, TX. At all sites, increases or decreases in the various observed taxa were considered to be due to normal phenological events that occurred during the course of 6- to 12-week course of the studies (Petty et al, 1998).

At the California site, the most common taxa observed at the end of the study were Libellulidae, Gastropoda, *Daphnia* spp. Aeshnidae, Aetidae, Coenagrionidae, Chironomidae, Ostracoda, Gammaridae, *Conchostaca* spp. and Oligocaheta. However, high frequency of most of these taxa were not seen prior to treatment with triclopyr TEA at the Elk Grove site. Only Gastropoda and Notonectidae were seen at high frequency prior to treatment.

At the Missouri site, there was a slight decrease in the number of invertebrate taxa found in treated ponds. Prior to treatment there was an average of 12 taxa and after treatment only 11.5 taxa were found. The number of samples with invertebrates in treated ponds was 8% lower 11.5 weeks after treatment, but the decrease was even greater in the control ponds with a 20% decrease. Taxa that were prevalent at the Columbia site before and after treatment with triclopyr included *Daphnia* spp. other

Cladocera, Notonectidae, Lestidae, Libellulidae, Ephemeroptera, *Haliplus* spp. and *Physa*.

At the Texas site, there was a distinct shift in the aquatic invertebrate community in both treated and untreated ponds during the 6-week course of the study. This shift in community was most likely due to increases in temperature and was not due to the direct impact of triclopyr. These increases were mirrored by increased levels of green algae in both treated and control ponds. Prior to treatment the dominant invertebrate taxa were tadpole shrimp (*Apus* sp.), fairy shrimp (*Eubranchipus* sp.) and the water flea (*Daphnia* sp.). Six weeks after treatment the dominant taxa were pond snails (*Physa* sp.), juvenile dragonflies (Libellulidae sp.) and phantom midges (Chaoboridae).

The data from the field confirms the conclusions arrived at from the risk assessment. Aquatic invertebrates from either the water column or sediment are not likely to be affected by the direct or secondary impacts of triclopyr TEA. Treatment with triclopyr TEA is not likely to directly or indirectly impact water quality when applied at the rates recommended on the label. Although changes in water quality with subsequent changes in the frequency and diversity of species occurs during the course of the treatment season, similar changes were observed in both treated and control plots.

- **Chronic risk assessment**

The typical environmental concentrations of the pesticide that the biota will be exposed to for “chronic” periods of time is determined as follows: Chronic exposure is typically considered to be 21 to 28 days. However, what is considered chronic exposure for a species, in part depends on the length of its life-cycle. For example, a chronic exposure for *Ceriodaphnia dubia* may be considered to be 4 to 7 days since this organism is able to complete its full life-cycle within this time frame. However, a chronic exposure for *Daphnia magna* is generally considered to be 21 to 28 days since it takes this much time for this species to go from a neonate to the completion of its reproductive period. Fish on the other hand, can take 30 to 90 days to go through a sensitive portion of their life-cycle, which is generally from egg to free-swimming fry.

For triclopyr, the typical environmental concentration that fish and most invertebrates will be exposed to for chronic periods is fairly low. Therefore, the 28-day TWA-EEC = 0.89 to 2.4 ppm a.e. assuming a maximum use rate application of 2.5 to 6.6 ppm a.e. and an aquatic dissipation half-life for triclopyr of 7.5 days. However, since triclopyr TEA displays no significant chronicity, EECs that should be used may be closer to the concentration (EEC = 2.5 to 6.6 ppm a.e.) than the TWA-EEC after 28 days of dissipation.

Even the most susceptible species of fish will not be adversely impacted by chronic 28- to 31-day exposure to triclopyr. The long-term level of concern is less than 1.0 as demonstrated by the chronic risk quotient; RQ = EEC/MATC = 0.16 = 6.6 ppm a.e/41ppm a.e. for fathead minnow. The concentration of 6.6 ppm a.e. was selected as a potential worst case when the targets are riparian, shoreline or wetland weeds treated with 9 lbs a.e./acre. Other treatment practices for the control of submerged weeds (2.5 ppm a.e.) or emerged weeds (6 lbs/acre = 4.4 ppm a.e.) will give risk quotients that are somewhat less (0.06 to 0.11) than the values presented here. If an estimate is made for the MATC of the most sensitive species based on the acute to chronic ratio (3.0) for fathead minnow, the MATC for rainbow trout would be 27 ppm a.e. (82 ppm a.e./3). Since this predicted MATC is significantly higher than the EEC on the day of application, one can conclude that the fish biota will not be adversely impacted by triclopyr when applied at the maximum use rate (RQ = <1.0 = 0.24 = EEC/MATC = 6.6 ppm a.e../27 ppm a.e.). This conclusion can generally be assumed to be valid since the chronic tests on which it is based are longer than 28 days

Chronic risk to triclopyr may be an issue with the invertebrate species. In particular, the estuarine bivalve (*Crasostrea virginica*) may be at risk when exposed chronically to triclopyr TEA. The chronic 21-day MATC (35 ppm a.e.) indicates that *Daphnia magna* will not be impacted when the EEC on the day of applications is used to determine the risk quotient. This lack of chronic impact is predicted since the chronic risk quotient is lower than the level of concern (1.0); RQ = EEC/MATC = 0.18 = 6.6 ppm a.e./35 ppm a.e. on *Daphnia magna*. If an estimate is made for the MATC of the most sensitive species based on the acute to chronic ratio (10.7) for *Daphnia magna*, the MATC for red swamp crayfish would be >9.6 ppm a.e. (>103 ppm a.e./3). Since this predicted MATC is significantly higher than the EEC on the day of application, one can conclude that the aquatic invertebrate arthropod (crustacean) biota will not be adversely impacted by triclopyr when applied at the maximum use rate (RQ = <1.0 = <0.69= EEC/MATC = 6.6 ppm a.e../>9.6 ppm a.e.).

Other more susceptible species indicate that the estuarine bivalve (eastern oyster = *Crassostrea virginica*) may be adversely impacted in its growth and reproduction since the predicted chronic MATC (2.1 ppm a.e.) is less than the highest concentrations that this species is likely to encounter shortly after application (2.5, 4.4 to 6.6 ppm a.e.) Even if the 21-day TWA-EEC (1.1, 1.9 or 2.9 ppm a.e.) for control of submerged, emerged or riparian wetland weeds, the higher concentration of triclopyr yields a risk quotient that is higher than the level of concern (1.0); RQ = TWA-EEC/MATC = 1.4 = 2.9 ppm a.e./2.1 ppm a.e. However, since triclopyr is not applied directly to estuaries and extensive dilution is likely to occur due to advection, dispersion and tidal action, it seems unlikely that concentrations higher than the predicted chronic MATC (2.1 ppm a.e.) are likely. Therefore, invertebrates with susceptibility to triclopyr similar to that of the eastern oyster are not likely to be chronically affected.

Concentrations of triclopyr in deeper water (6 feet deep) due to direct overspray or leaching of 6.0 lbs a.e./acre or 9.0 lbs a.e./acre (0.27 to 0.55 ppm a.e.) is a more likely scenario for chronic exposures with both fish and aquatic invertebrates. Those initial EECs are much less than the predicted chronic EC_{50} for the most sensitive specie of fish (27 ppm a.e. for rainbow trout) or invertebrate (2.1 ppm a.e. for eastern oyster embryo/larvae). Therefore, chronic exposure to triclopyr is unlikely to adversely impact the animal biota in a manner that will affect growth or reproduction.

True chronic field studies have not been conducted with fish. However, based on short term field studies (<21 days), it does not seem likely that fish will be adversely impacted when exposed chronically to triclopyr. The field studies (described under acute risk assessment and in Section 4.3.2.3) showed no significant impact on the frequency of occurrence of aquatic invertebrates. Therefore, it is unlikely that aquatic invertebrates found in the water column or sediment would be adversely impacted by the direct or indirect action of triclopyr.

Summaries of Risk Assessments used in this section are provided in Table 19.

4.3.3 Triclopyr Potential Impacts to Terrestrial Wildlife and Plants

The goal of this portion of the document is to discuss the effects of single applications/exposures and chronic applications/exposures to terrestrial wildlife (birds and mammals) and terrestrial plants exposed to the aquatic herbicide containing triclopyr (Renovate®). In addition, possible effects on the food chain and threatened and endangered species will be discussed as well as ways to mitigate exposure of these organisms to the aquatic uses of triclopyr. The information presented summarizes toxicological studies to determine the effects of triclopyr containing product Renovate® on plant and animal species.

4.3.3.1 Effects on Amphibians

No laboratory work was conducted on the effects of triclopyr TEA against amphibians. Triclopyr BEE killed or temporarily paralyzed *Rana pipiens*, *Rana clamitans* and *Rana catesbeina* tadpoles at concentrations as low and 2.4 to 4.8 ppm a.i. (Berril et al, 1984). Concentrations of 1.2 ppm a.e. also temporarily paralyzed tadpoles of all test species. However, if the embryonic amphibians survived, exposure to triclopyr BEE did not appear to effect hatching, success, and avoidance of mechanical stimulus or growth. Since triclopyr BEE has similar acute toxicity against fish [(LC_{50} = 0.65 to 2.4 ppm (EPA RED, 1998)], the toxicity of triclopyr BEE to amphibians was also anticipated to be high. However, it is not likely that triclopyr TEA will adversely impact these species at similar concentrations. It is anticipated that amphibians will be affected by triclopyr TEA both acutely (LC_{50} = 82 to 182 ppm a.e. = 114 to 254 ppm a.i.) and chronically (MATC = 27 to 61 ppm a.e. = 38 to 93 ppm a.i.) at concentrations similar to that affecting fish. What little data is available from the field indicates that *Rana pipiens* adults and tadpoles remain common 11 weeks after treatment of the Columbia, MO pond site at rates of 2.5 ppm a.e. (Petty et al, 1998).

4.3.3.2 Effects on Terrestrial Animals (Birds, Mammals and Insects)

Studies have been conducted to assess the toxicity of technical grade triclopyr and the triclopyr containing product Renovate® on various animal groups. Acute oral (LD_{50}), acute dietary (LC_{50}) and chronic dietary studies are presented.

4.3.3.2.1 Acute Effects on Birds

Acute oral data are available for triclopyr acid and the triethylamine salt in the mallard duck (Table 21). The acute oral LD_{50} for triclopyr acid in mallard ducks was 1,698 mg/kg. The acute oral LD_{50} for the triethylamine salt ranged from 1,698 to 3,176 mg/kg in two different studies. These data indicate that triclopyr acid is slightly toxic and that the triethylamine salt is slightly toxic to practically non-toxic to birds when orally dosed.

Acute dietary (LC_{50}) data is available for triclopyr acid and the triethylamine salt for several different species of birds. The LC_{50} for triclopyr acid is 5,620 ppm in mallard ducks, 3,272 ppm in Coturnix quail and 2,934 ppm in bobwhite quail. The LC_{50} for the triethylamine salt was >10,000 ppm in the mallard duck and 11,622 ppm in the bobwhite quail. These data indicate that triclopyr acid is slightly to practically non-toxic and that the triethylamine salt is practically non-toxic to birds when consumed in the diet.

4.3.3.2.2 Chronic Effects on Birds

One generation reproduction (in feed) studies were performed on both bobwhite quail and mallard ducks. The no observable effect concentration (NOEC) for triclopyr acid in the bobwhite quail is 500 ppm. The NOEC for mallard ducks is 100 ppm triclopyr acid. This data indicates that reproduction of birds may be affected at levels greater than 100 ppm (RED).

4.3.3.3 Acute Effects on Mammals

Acute oral rat data is available for both triclopyr acid and its triethylamine salt. The LD_{50} values for the acid range from 630 mg/kg in female rats to 729 mg/kg in male rats (EPA RED, 1998). The LD_{50} for the triethylamine salt is 1,847 mg/kg in male and female rats. This data indicates that both triclopyr acid and triclopyr triethylamine salt are slightly toxic to mammals.

4.3.3.3.1 Subchronic and Chronic Effects on Mammals.

A 13-week sub-chronic rat dietary toxicity study was conducted using triclopyr acid. The systemic NOEL for this study was 5 mg/kg/day based on histopathological changes in the kidneys at the next highest dose level (20 mg/kg/day). The systemic NOEL for a 228-day dog dietary study, using triclopyr acid, was determined to be 10 mg/kg/day. The NOEL was based on decreased body weight gain in male dogs, decreased hematological parameters in male dogs, changes in clinical chemistry in male and female dogs, and liver histopathology in male and female dogs at the next highest dose level tested (20 mg/kg/day) (RED).

A chronic mouse toxicity/carcinogenicity study was conducted using triclopyr acid. The no observable effect level (NOEL) for male mice was 28.6 mg/kg/day and 26.5 mg/kg/day for female mice. These findings were based on decreased body weight gain at the next highest dose level (143 mg/kg/day males and 135 mg/kg/day females (RED). A two-generation rat reproduction study was performed using triclopyr acid. The reproductive/systemic NOEL for the rat reproduction study was found to be 25 mg/kg/day based on decreased litter size, decreased body weight and weight gain, and decreased survival of the F_1 and F_2 litters at the next highest dose level (250 mg/kg/day).

A 2-generation rat reproduction study was conducted using triclopyr acid (Vedula et al, 1995). The parental NOEL was found to be 5 mg/kg/day and the NOEL for fertility and neonatal toxicity was found to be 25 mg/kg/day.

A one-year dietary dog study was conducted using triclopyr acid (Quast et al, 1988). The NOAEL for this study was 5.0 mg/kg/day, which was the highest dose level tested.

4.3.3.4 Mitigation of Effects on Birds and Mammals

- **Mitigation measures specific to triclopyr products**

  There are two common routes of exposure of livestock and terrestrial wildlife to aquatic applications of Renovate®. The two routes are exposure through drinking water treated with products containing triclopyr or eating aquatic plants, fish or other aquatic organisms from the treatment site. Based on the acute and chronic studies listed above, triclopyr and its products used as aquatic herbicides do not pose a significant acute or chronic risk to wild birds or terrestrial mammals. Many studies have been run on these products to ensure their safety to wildlife and the label directions and warnings reflect the results of these studies. Therefore, if the chemicals are applied according to the label, the effect on terrestrial wildlife should be minimal.

- **General mitigation measures**

  Although triclopyr products used as aquatic herbicides do not pose a significant risk to terrestrial wildlife, the following measures should be considered prior to all aquatic herbicide applications. One possible mitigation measure would be not allowing applications if large populations of birds use shorelines or islands in the water body to be treated for nesting until after nesting is complete. Another mitigation measure would be to time applications to avoid migratory waterfowl and other bird species that use certain water bodies during migration. Efforts to avoid effects on migratory and nesting birds would best be coordinated between the permit writer and The Washington State Department of Fish and Wildlife (WDFW) prior to granting the permit.

4.3.3.5 Possible Effects on the Food Chain

The potential of triclopyr to bioaccumulate in birds and mammals has not been well studied. However, it is unlikely that bioaccumulation will occur due to triclopyr's low K_{ow} and its rapid binding to soil/sediment. Adverse effects on the food chain are also unlikely because of the relatively high LC_{50} and LD_{50} values reported and the low no observable effect levels seen in chronic studies with birds and mammals.

4.3.3.6 Effects on Endangered Terrestrial Plants, Birds and Mammals

A list of endangered terrestrial plants, birds and mammals is located in Table 23. Minimal effects to these organisms are expected from application of aquatic herbicides containing triclopyr. It should also be noted that Renovate® appears to be of similar toxicity to terrestrial organisms. Mitigation of possible effects on listed endangered species is best accomplished by following the mitigation sections for terrestrial plants, birds and animals. As stated previously, the best way to mitigate possible effects on all terrestrial species is to follow the directions listed on the label.

Other mitigation measures involve the contact of WDFW by the issuer of the permit to ascertain if any endangered species may be affected by the application of the chemical to the water body in question. Questions asked by the permit granter would ascertain if any resident endangered bird or animal species are known to use the water body in question or its shorelines or islands as breeding or forage areas, or if the application coincides with the migration of any endangered species. If endangered species are present, mitigation measures may involve postponing application until after the breeding season or postponement of application until after migration of the species in question. Use of an alternate means of control (i.e. mechanical) may also be an option if the risk is determined to be too great to the species in question.

4.3.3.7 Effects on Terrestrial Plants

- **Acute effects of triclopyr on terrestrial plants**

  Triclopyr is a selective systemic herbicide used mainly for control of woody and broadleaf plants along rights-of-ways, in forests, on industrial lands, and on grasslands and parklands (Extoxnet). Federal registration of the triethylamine salt of triclopyr is being sought for the control of invasive aquatic weeds such as Eurasian watermilfoil, purple loosestrife, water hyacinth and alligator weed. Adverse effects to terrestrial plants depend on a wide variety of factors including application rate and number of applications, soil absorption and the susceptibility of the species in question.

  Acute risk and endangered plant species levels of concern from runoff of triclopyr triethylamine salt during ground application are exceeded at ≥ 9.0 lb a.e./A (non-target plants inhabiting adjacent acreage) and ≥ 1.5 lb a.e./A (non-target plants inhabiting semi-aquatic areas) (Triclopyr RED). Aquatic use rates for this material are well below the use rates listed above. Therefore, little or no harm to non-target terrestrial plants is expected due to either over spray or the use of triethylamine salt treated irrigation water.

  A seedling emergence test conducted by Schwab (1993) found that triclopyr significantly effected tomato plant emergence at 0.00015, 0.0041, 0.0123 and 0.037 lb a.i./A. Barley, corn and sorghum were also effected at these levels. Shoot length and shoot weight were also effected (Table 22).

- **Mitigation of the effects on terrestrial plants**

  The main route of exposure for terrestrial plants to aquatic herbicides are through spray drift and the use of treated water as irrigation. Aerial applications of Renovate® are allowed by helicopter according to the technical bulletin. However, they are not allowed when conditions favor drift to sensitive areas. The bulletin further states that drift should not be permitted onto any desirable broadleaf plants as injury may occur. Therefore, drift to adjacent terrestrial areas should be minimal. In order to mitigate against possible problems with irrigation water, the technical bulletin does not allow irrigation for two weeks after application. The proposed Garlon® 3A label does not allow irrigation for 120 days after treatment of water that may be used for irrigation.

4.3.3.7.1 Acute effects on Honey Bees

An acute contact toxicity honey bee study was performed using triclopyr acid (Dingledine, 1985). The contact LD_{50} of triclopyr acid was found to be >100 micrograms/bee. This finding indicates that triclopyr acid is relatively non-toxic to bees (Table 21).

4.4 ADDITIONAL POTENTIAL DIRECT AND INDIRECT IMPACTS OF HERBICIDE USE ON WETLAND ENVIRONMENTS

Summary: The presence of triclopyr products at concentrations effective against weeds in wetland environments may adversely effect these environments. Dilution effects should mitigate the effects of triclopyr so that it does not effect non-target aquatic plants or non-target animals in marsh, bank and estuarine areas. The presence of triclopyr in the lotic environment, due to outflow from a lake or pond, may cause the destruction of aquatic plants favorable to the production of appropriate habitat for sunfish, minnows and bass. The subsequent habitat, with a low level of areal aquatic weed cover and a benthos consisting primarily of sand and gravel would be more appropriate to the production of salmonids. However, most species of non-target aquatic plant are tolerant to the effects of triclopyr and will thrive after the removal of Eurasian watermilfoil. This is particularly so in riverine areas, and these non-target native plant species are often more susceptible in ponds where the inflow and outflow of water is minimal.

The estuarine environment may be affected by the use of triclopyr. **.** *One of the more susceptible species of invertebrates is the eastern oyster (*Crassostrea virginica*) with an acute* LC_{50} *ranging from 22 to 41 ppm and a predicted chronic MATC of 2.1 to 3.8 ppm a.e. However, this species is not likely to be affected in the field due to dilution from advection, dispersion and tidal flow and the fact that triclopyr TEA is not typically applied to estuaries.*

Failure to control emersed, floating, marginal and bank weeds can cause the native vegetation to be crowded out producing dense monoculture stands of noxious and invasive weeds, leading to the degradation of natural habitats and an economic burden for residents and aquatic weed control professionals who must keep water flowing or navigable.

Except for grasses, most crop plants may not be able to withstand treatment of irrigation water with triclopyr at typical use rates. Since irrigated crop studies have not been conducted, there is a 120-day use restriction after application of triclopyr to water that may be used for irrigation. Also due to the lack of irrigated crop studies, triclopyr may be applied to drainage ditches or canals only in non-irrigation situations. If the water use restrictions noted on the label are followed, treated water may be used for household sources and to water livestock. However, the proposed current label does not specify any use restriction for the watering of livestock.

Residue levels on shellfish may be higher than the proposed fish/shellfish tolerance of 0.2 ppm a.e. Therefore, a shellfish harvest restriction of up to 3 weeks may be necessary.

Because of the manner in which triclopyr products are applied, significant impact to other wetland environments is unlikely. There may be some tendency for drift into other wetland environments or a flow of water into estuarine, palustrine, riparian, lentic or lotic environments. However, it is not anticipated that the impact would be measurable due to dilution effects, as treated ponds, lakes, and canals normally flow into streams and rivers and ultimately into estuaries.

4.4.1 Estuarine (Intertidal) Environments

Water from a stream or river containing triclopyr may flow into an estuary. However, dilution effects from the water already present in the estuary and diurnal tides should dilute triclopyr to levels where it is not significant in the water column. Although some estuaries contain a considerable amount of sediment, triclopyr has not been observed to bind to sediment since it has a low soil water adsorption coefficient (Freundlich Kd = 0.165 to 0.975 mL/g) even in soils that have a fairly high organic carbon content (Woodburn et al, 1988). It has been demonstrated that triclopyr in sediment is generally low (<1.0 ppm a.e.) on the day of application and generally dissipates to concentrations below 0.01 ppm a.e. in 14 to 42 days. Furthermore, the concentration in sediment is uniformly lower than the concentration in water. Therefore, it is unlikely to cause adverse impact on estuarine organisms (Petty et al, 1998; Getsinger et al, 2000 and Green et al, 1989). However, while the metabolite of toxic concern (TCP) is also normally observed to remain below the limit of detection in sediment, it can be seen at sediment concentrations as high as ~0.1 ppm for up to 2 weeks and can remain in water at concentrations of ~0.015 ppm for up to several days after application.

No bacterial species have been noted to degrade triclopyr. However, triclopyr acid degrades slowly (DT50 = 142 days) and produces 5% of the metabolite TCP after 30 days incubation under aerobic aquatic conditions and produces 25% of the metabolite TCP after 365 days incubation under anaerobic aquatic conditions. Triclopyr also degrades fairly rapidly on soil with half-lives ranging from 8 to 18 days and produces 8% to 26% of the metabolite TCP in less than 30 days under aerobic conditions. Since triclopyr acid does not hydrolyze at pHs ranging from 5 to 9, the data from aerobic soil, aerobic aquatic and anaerobic aquatic studies is indicative of microbial degradation. Although species of microbes that degrade triclopyr are not indicated in the literature, it seems possible that species of microorganisms that degrade 2,4-D are also likely to degrade triclopyr. These species include *Achromobacter*, *Bordetella*, *Xanthobacter*, S*treptomyces*, *Aspergillus*, *Corymebacterium*, *Nocardia*, *Acrobacter*, *Alcaligenes*, *Arthrobacter*, *Flavobacterium* and *Pseudomonas* (Aislabie and Lloyd-Jones, 1995; Washington State, 1993; Smith et al, 1994). Other microbes that may degrade triclopyr (since they are known to degrade 2,4-D) include the fungae *Dichomitus squalens* and *Phaerochaete chrysosporium* (Vijay et al, 1997) and 72 isolates of actinomcycete (Han and New, 1994).

For triclopyr, the estuarine/marine/euryhaline organisms had LC_{50} or EC_{50}s that ranged from 22 ppm a.e. for eastern oyster embryos and larvae to >314 ppm a.e. for the fiddler crab (*Uca pugilator*). Other species of estuarine arthropod that are fairly tolerant of triclopyr TEA include grass shrimp (96-hour EC_{50} = 234 ppm a.e. and pink shrimp (96-hour EC_{50} = 281 ppm a.e.)(Table 18). A fish typically found in estuaries is the tidewater silverside (*Mendidia beryllina*), which has a 96-hour LC_{50} of 148 ppm a.e. Other species of fish, which are found in either freshwater or saltwater, may at times be found in estuary environments. These species include the several *Oncorhynchus* salmon species (96-hour LC_{50} = 96 to167 ppm a.e.) and the steelhead trout (96-hour LC_{50} = 82 to 151 ppm a.e.). Estuarine shrimp and other small estuarine species are often tested for toxicity because of their importance in the aquatic food web, their great abundance and sensitivity to pollution and pesticides.

Some of the estuarine/marine species are more susceptible than the freshwater species to a variety of pesticides. However, of the species tested only the eastern oyster appears to be more susceptible than freshwater species. Whether or not the eastern oyster is classified as an organism at potentially high risk depends on the paradigm used. If EPA's risk assessment methodology is used, it is considered an organism at risk but probably not high risk since its LC_{50} (22 to 41ppm a.e.) is typically not higher than 10-times the initial EEC (2.5 to 6.6 ppm).

In general, sediment organisms like the eastern oyster would have somewhat reduced risk since triclopyr would be extensively diluted by the time it reached an estuary, and triclopyr does not accumulate in the sediment. Furthermore, Green et al (1989) conjectured that animals dug into the sediment would have a reduced exposure risk from triclopyr dissolved in the water column. Such species could include bivalves like the eastern oyster as well as the freshwater species (freshwater clams and red swamp crayfish) that were studied by Green et al.

4.4.2 Palustrine (Marshy) Environments

Extensive growth of rooted aquatic macrophytes such as rushes and cattails may effectively dam a marsh and increase the depth of the palustrine system by several-fold. In this way aquatic macrophytes assist in spreading waters onto the surrounding land to increase its fertility and provide additional areas for fish and amphibians to feed and spawn (Goldman & Horne, 1983). It is noteworthy that rushes (*Scirpus*) and cattails (*Typha*) appear to be resistant or tolerant to the effects of triclopyr (Woodburn et al, 1993). Even without flooding, these plants may have an effect on habitat suitability for wild birds, mammals and other terrestrial organisms.

The dominant plants found in palustrine environments are emersed (emerged). While most emerged species are not affected significantly by triclopyr, American lotus *(Nelumbo lutea*), the water lilies (*Nymphaea odorata* and *Nuphar* spp.), waterprimrose *Ludwigia uruguayensis*) and possibly purple loosestrife (*Lythrum salicaria*) can be severely affected since they are species for which efficacy is claimed (proposed Garlon® 3A label). Most emersed plants are not likely to be adversely impacted at the concentrations of triclopyr used to control fully aquatic weeds. However, floating (*Eicchornia crassipes*) and rooted submersed plants (*Myriophyllum* spp. and *Hydrocotyle* spp.), that are typically found in a palustrine environment may be impacted by water that enters these areas from lakes and ponds. For example, as expressed in the label and in the modeling work done by Ritter and Peacock (2000) a setback distance of 200 to 2,000 feet may be necessary when triclopyr is used to control floating/emerged or submerged aquatic weeds in order to assure that 0.5 ppm a.e. triclopyr TEA does not come into contact with a given area. Also up to 21 days must pass in a pond treated with triclopyr at the maximum use rate in order to assure that there is no more than 0.5 ppm a.e. triclopyr TEA in the treated water. These distances and restrictions are important since it has been observed that concentrations of triclopyr TEA as low as 0.25 ppm a.e. can damage *Myriophyllum* spp. when the average exposure time is two or more days and 100% control of *Myriophllum spicatum* can occur after 96-hour exposure (Netherland and Getsinger, 1993 and Getsinger et al 1997). It is unclear exactly how high the triclopyr concentrations must be to damage native plant species but initial triclopyr concentrations of 2.5 ppm a.e. that remained at levels of 1.0 ppm a.e. or higher for 7 to 14 days have been known to adversely impact coontail (*Ceratophyllum* spp.), Eurasian watermilfoil

(Myriophyllum spicatum), southern naiads (*Naja guadalupensis*), and American waterweed (*Elodea canadensis*) in water impounds (ponds) located at Elk grove, CA, Columbia, MO or Lewisville, TX (Petty et al, 1998). If these rooted macrophytes are destroyed due to a herbicide, there will be less tendency for the marsh to flood and therefore, potential habitat will be lost to fish and amphibians. Also, if these plants are lost, and flooding does not occur, loss of suitable habitat for wild birds and mammals may occur.

4.4.3 Riparian (Margin and Bank) Environments

Triclopyr products may be used to treat the submerged margins of lakes and ponds to eliminate weeds that interfere with recreational use. Triclopyr is also used to control broadleaf annual and perennial weeds and woody brush along rights-of-way, non-irrigation ditch banks, and floating, emerged, marginal and bank weeds on reservoirs, ponds and lakes.

The application rates of these herbicides have the potential to impact any non-target broadleaf species that they come in direct contact with. The rate of application as a spot spray to non-aquatic or bank weeds is typically 2 to 3 gallons Renovate® or Garlon® 3A/acre in 20 to 100 gallons of water. Non-ionic surfactants like X-77 should be used according to the surfactant label. Enough water should also be added to assure completed wetting of the treated foliage. The Garlon® A label specifies which species of non-aquatic weeds are controlled. For best results, the target weeds should be young, actively growing annual broadleaves, perennial broadleaves or woody brush. Difficult weeds (Purple loosestrife, waterhyacinth, alligatorweed, other emerged and floating herbaceous weeds and woody plants) may require repeat treatments to control re-growth and plants missed in previous operations, but the annual maximum use rate should not be exceeded for any specified control measure (submerged, emerged, floating or terrestrial weeds).

For terrestrial weed control, tank mix 0.5 to 1.0 gallon of Garlon® 3A or Renovate® with a 0.25 to 0.5 gallon of 2,4-D 3.8 lb amine or 2,4-D low volume ester or Tordone® 101 Mixture herbicide with enough water to make 100 gallons of spray. This spray mixture should be applied at volumes of 100 to 400 gallons of total spray per acre depending on size and density of woody plants. Similar mixtures may be used to control broadleaf weeds, but the rate of application is slightly different with 0.33 to 1.5 gallons Garlon® 3A tank mixed with 0.5 to 1.0 gallon of the tank mix partner. The total volume of spray mix may vary somewhat according to the application, but typically 20 to 100 gallons of total spray mixture may be applied to an acre of weeds to be controlled. Triclopyr has particular utility in controlling a variety of other emergent and terrestrial species which proliferate in wetland habitats. Wetlands may include flood plains, deltas, marshes, swamp bogs and transitional areas between upland and lowland sites. Wetlands may occur within forests, non-crop sites, wildlife habitat restoration and management areas and similar sites. Also included as wetlands are areas adjacent to or surrounding domestic water supply reservoirs, lakes and ponds. Non-native riparian weeds may grow in dense monoculture stands that provide poor habitat for native wildlife. In producing thick stands, these weeds may chokes out waterways, slowing flow and promoting siltation. Invasion of these noxious weeds results in degradation of natural habitats for native vegetation and wildlife as well as causing economic burden on farmers and vegetation management professionals who must keep irrigation water flowing and aquatic weeds in recreational areas under control.

Triclopyr TEA can be used under a wide range of environmental conditions to control woody plants and broadleaf weeds in forests and terrestrial non-crop sites. As discussed before, these products may be applied directly to the water of ponds, lakes, reservoirs, marshes and wetlands including banks and shores adjacent to these sites (Garlon® 3A proposed label, 2000).

Application rates for control of non-aquatic weeds (emerged and wetland terrestrials) has been previously described. For the control of Eurasian watermilfoil and other susceptible submerged aquatic weeds, Renovate® and Garlon® 3A may be applied at concentrations of 0.75 to 2.5 ppm a.e. to water bodies which have little or no continuous outflow. Higher rates are recommended in areas of greater water exchange and more than one application may be required to control submerged weeds in these areas. However, the total application of these products should not exceed 2.5 ppm a.e. for the treatment area per annual growing season. For control of floating or emerged weeds, 0.5 to 2 gallons formulation/acre (1.5 to 6 lbs a.e./acre) may be used. Higher rates should be used when plants are mature or when weed mass is dense or a difficult-to-control species is present. Repeat treatments are necessary to control re-growth and plants missed in previous operations. However, the total application of these products to control floating and emerged weeds should not exceed 2 gallons formulation/acre per annual growing season.

Triclopyr has been used experimentally in Washington at Loon Lake in 1998, the Okanogan River floodplain in 1999, Mason Lake in 1999, Diamond Lake in 1999, Thomas Lake in 1999, the Little Pend Oreille Lakes in 1999 and Liberty Lake in 1999. This product has been applied under EPA Experimental Use Permit No. 62719-EUP-1 using an experimental label for Renovate® issued by DowElanco. The target weed was Eurasian watermilfoil for all sites except the Okanogan River floodplain where it was purple loosestrife. Although the Renovate ® experimental label indicates that Eurasian watermilfoil may be controlled at concentrations ranging from 1.0 to 2.5 ppm a.e., the maximum use rate and maximum treatment areas specified in the permits are site specific. The degree of weed control achieved at these treatment sites was not available at the time this document was written. However, Eurasian watermilfoil and purple loosetrife has been reported to be adequately controlled in the Pend Oreille River and Moses Lake wetlands, respectively (Getsinger et al 1997; Netherland and Getsinger, 1993 and Gardner and Grue, 1996). The control of Eurasian watermilfoil in the Pend Oreille River was effective for up to 3 years due to the establishment of a robust and diverse native plant community, which through competition delayed the reestablishment and dominance of Eurasian watermilfoil. However, the control of purple loosestrife was only adequate during the year that Garlon® 3A was applied, and growth of new stems appeared to be stimulated one year after application.

Triclopyr products (Renovate® and Garlon® 3A) may also be used for other plant control including forest management applications and control of weeds in Christmas tree plantations. It may also be used as a directed spray for the control of weeds in grazed areas and in areas used to grow green forage or hay. Green forage should not be fed to lactating dairy animals for 14 days after treatment with up to 0.67 gallons formulation /acre and should not be fed to lactating dairy animals until the next growing season if 0.67 to 2 gallons formulation/acre is used to treat this crop. Dry forage should not be fed to dairy animals until the next growing season, and other livestock should not be fed dry forage for 7 days after treatment with up to 0.67 gallons formulation/acre. Other livestock should also not be fed dry forage for 14 days after treatment of 0.67 to 1.33 gallons formulation/acre. If greater than 1.33 gallons is used to treat dry forage crops, other livestock should not be fed this commodity until the next growing season. Livestock should be withdrawn from grazing treated grass or consumption of treated hay at least three days before slaughter if the most recent treatment has been during the current growing season. As a general rule, the residue tolerance for triclopyr on grass forage and grass hays is 500 and 200 ppm a.e., respectively. Although the proposed Garlon® 3A label specifies the above treatment rates, the EPA RED (1998) states that "…the maximum yearly use rate must be restricted to 0.33 gallons formulation/acre (1.0 lb a.e./acre)" for uses on grass forage.

Any non-target plants and animals have a potential to be impacted by triclopyr products as described in Sections 4.2.3.1, 4.2.3.2, 4.3.3.1, 4.3.3.2 and 4.3.3.4. Please review these sections for information on triclopyr's acute (Tables 2, 14, 15, 16, 17 and 18) and chronic (Tables 2, 19 and 20) effects in non-target aquatic plants and animals.

4.4.4 Other Wetland Environments

Pasture, which is partially flooded, may be impacted by triclopyr treated waters that caused the flooding. Established terrestrial grasses may be irrigated with treated irrigation water immediately after treatment of that water with the maximum use rate of triclopyr. However, since no irrigated crop studies have been conducted, treated water may not be used for 120 days after treatment with triclopyr TEA. Many sensitive plants have been affected by triclopyr including grapes, tobacco, vegetable crops, flowers and other desirable broadleaf plants. Non-target terrestrial plants (endangered species) and plants in semi-aquatic areas are likely to be adversely impacted since a 1% drift from treatments at 6.0 and 9.0 lb a.e./acre produce risk quotients that exceed the level of concern (1.0). Furthermore, sunflowers are damaged at a treatment rate of 0.005 lb a.e./acre, which is much below the concentration (0.06 to 0.09 lb a.e./acre) of triclopyr likely to be encountered from 1% drift (Table 9)(EPA RED, 1998). Section 4.2.5 deals with the effects of irrigation water, agricultural sprays and flood water.

4.4.4.1 Lentic Environment

Potential impacts on lentic and lotic environments as to the chemical ecology were discussed extensively in Section 4.2.3.1. Effects on the biota in these environments were discussed extensively in Section 4.3.

4.4.4.2 Lotic Environment

The lotic environment can be influenced by the presence of triclopyr in water from a lake or pond outlet. If triclopyr is present at levels that control weeds and the outlet gate is closed, a type of habitat favorable to sunfish and amphibians will develop. If the outlet gate is open, another type of habitat more favorable to salmonids may develop. If protracted (seasonal) contact with water containing triclopyr at concentrations of as low as 2.5 ppm c.e. occurs, *Ceratophyllum* spp., *Elodea canadensis* and *Najas guadalupensis* may be controlled or adversely impacted (Petty et al, 1998). Although these species appear to be tolerant to triclopyr in riverine and other situations where significant water flow occurs (Getsinger et al, 1997 and Netherland and Getsinger, 1993) in impounded (pond water) situations, these species may be adversely impacted. Other species of native aquatic plants appear to be unaffected in impounded water situations. Species of plants that remain frequent in impounded water situations include E*locharis* spp., *Chara* spp., certain other *Najas* spp., and most green algae and diatoms. Most blue-green algae species are adversely impacted to some degree in water impoundments.

- **Closed outlet gate or absence of triclopyr**

  If the outlet gate from a pond or lake to a river or stream remains closed, dense growths of rooted aquatic macrophytes may effectively dam rivers and streams and increase the depth of the lotic system by several-fold. In this way the aquatic macrophytes assist in spreading waters onto the surrounding land to increase its fertility and provide additional areas for fish and amphibians to feed and spawn (Goldman & Horne, 1983). Similar effects may occur if the lake or pond is not treated with triclopyr. The modeling work of Ritter and Peacock (2000) and the proposed Garlon® 3A label indicate that, in lotic systems, applying triclopyr to more than 16 acres at concentrations of 2.5 ppm a.e. requires a set back distance of up to 2000 feet. If this setback distance is maintained, triclopyr concentrations at intake pipes or outlet gates should remain below 0.5 ppm a.e. Even at these low concentrations, some species of plants (particularly Eurasian watermilfoil) are adversely impacted. However, some of the native species like *Najas* spp. and *Potamogeton* spp. are not adversely affected after germination in hydraulic channels (mesocosms) (Netherland and Getsinger, 1993).

- **Open outlet gate in presence of triclopyr**

  If water that contains triclopyr at effective concentrations passes through the outlet gate of a lake or pond into a river or stream, some of the rooted aquatic macrophytes may be destroyed. This can have a substantial impact during the next spate or high water event. Normal spring high flows, in absence of rooted aquatic macrophytes, can dig up and kill large numbers of benthic organisms while summer spates (uncommon in Washington) can completely denude streams of benthic biota.

  Most biota avoid spates either by migrating to calm back waters or by having life-cycles which are terrestrial or aerial at these times. However, when floods occur at unusual times the fauna may be severely depleted and require several years to recover (Goldman & Horne, 1983).

  Larger organisms, like salmonids, choose to ascend rivers or streams during spates or high water because there are fewer shallow water barriers. Severe floods are detrimental to smaller biota if they leave only inhospitable rocks and gravel. However, these increased water levels may improve fish migration by removing major obstacles. Adequate water levels can improve the environment for salmonid mating and egg survival by removing excessive silt. These benefits cannot occur if aquatic weeds have dammed the lotic system.

4.5 UNCERTAINTY ANALYSIS

Summary: The uncertainty analysis indicates that field studies often reflect the risk analysis used to generate the label. Models used since 1975 indicate that an acute risk quotient of <0.1 or a chronic risk quotient of <1.0 reflects safety of the product to exposed aquatic animals under field situations. An acute risk quotient is generated by dividing the short-term predicted environmental concentration (short-term EEC) by the acute LC50 of the most sensitive species of concern within the ecosystem. Providing a

10-fold safety factor will insure that only 0.01% to 4% of the animals with similar sensitivity will be adversely affected. Dividing the long-term EEC by the chronic MATC or chronic predicted NOEC for the most sensitive species generates a chronic risk quotient. The MATC is currently the preferred value as indicated in the Triclopyr RED (EPA RED, 1995). The MATC is the value that will be used if development, growth or reproductive effects are the end-points to be measured while the NOEC is used when mortality is the measured end-point. A safety factor is not necessary in chronic risk assessment since all animals with a similar sensitivity will also not be affected by exposure to chronic EECs for the compound being evaluated.

Triclopyr has been evaluated as having potential adverse impact on the larvae and spats of eastern oyster (RQ = 0.11 to 0.3). No other species tested was sensitive to triclopyr at concentrations (60 ppm a.e.) low enough to produce risk quotient values that were greater than the low level of acute concern (0.1) (Table 21). No field studies were conducted with eastern oyster. However, field studies with a variety of invertebrates including the freshwater clam, crayfish, branchiopods, copepods, ostracods, amphipods, arachnids, Daphnia *spp., other cladocerans, nematodes, gastropods, ephimeropterans and oligochaetes indicate that triclopyr does not directly impact the frequency or dominant species present in the water column or sediment (Gardner and Grue, 1997; Petty et al, 1998; Getsinger et al, 2000 and Green et al, 1989). Since the level of concern (0.1) was exceeded, the invertebrate biota was determined to be at potential risk. However, this level of risk was not confirmed by field tests. It was estimated that the risk to in-faunal estuarine invertebrates would be low since triclopyr is not labeled for estuarine applications. In-faunal species are also unlikely to be exposed to concentrations of triclopyr that are typically found in the water column, since the sediment does not adsorb triclopyr and it is likely to insulate in-faunal species somewhat from the exposure to triclopyr (Green et al, 1989). Since the high level of concern (0.5) was not exceeded in the risk assessment with eastern oyster larvae and spats, the classification and use of triclopyr TEA as a restricted use formulation should mitigate or prevent adverse impact to this species and species with similar sensitivity.*

However, even the most sensitive species of fish (rainbow trout) did not yield risk quotients that exceeded the level of concern. Since the level of concern (0.1) for the risk quotient was not exceeded, the fish biota was determined to be at low potential risk from exposure to triclopyr. In field tests with various non-game and game species of fish, no adverse impact was observed (Petty et al, 1998; Getsinger et al, 2000; Green et al, 1989 and Houtman, 1997).

There have been few chronic tests conducted with triclopyr and the data could possibly be judged to be insufficient for chronic risk assessment. Since triclopyr is rapidly dissipated, many authors feel that chronic exposure is not likely. Other authors believe that since the chronicity of triclopyr is low, the exposure concentration that occurs within the first 24 hours is likely to have the most important chronic impact on fish and invertebrates. The chronic risk quotient based on predicted MATCs and the initial application exceeds the level of concern (1.0) for the eastern oyster (chronic RQ = 0.66 to 3.1). Therefore, a few invertebrate species may be adversely impacted as to numbers, and reproductive capacity until the concentration of triclopyr falls below the level toxic to these invertebrates. Field studies with eastern oyster have not been conducted. However, the likelihood of exposure of estuarine bivalves to triclopyr TEA is considered to be minimal. Other species of invertebrates have not been chronically affected by exposure to triclopyr TEA and since the predicted MATC for these other species is above *the EEC, it is unlikely that invertebrate (arthropod, crustacean) biota will be adversely impacted.*

In no case did the chronic risk quotient based on predicted MATCs exceed the level of concern (1.0) for fish. Therefore, it is unlikely that the fish biota will be adversely impacted by chronic exposure to triclopyr. Field studies indicate that exposure to typical use rates will not directly effect the survivorship, numbers (fish-catch) or diversity in tests from 21 days to 84 days in length. However, these field tests do not address reproduction, growth, size structure or condition of the test organisms in the field (Petty et al, 1998; Houtman et al, 1997; Green et al, 1989; Foster et al, 1997; Woodburn et al, 1988 and Getsinger, 2000).

Classic laboratory risk assessment to determine the field safety of triclopyr was very effective as a predictive tool for risk management. The acute risk quotient with triclopyr is >0.1 for the most sensitive invertebrate species and <0.1 for all fish species that were tested for 48 to 96 hours. Treatment of ponds, lakes, reservoirs and rivers indicates that the impact of triclopyr on fish and amphibians is minimal and that no monitored species of invertebrate are affected by treatment with triclopyr TEA.

Secondary effects which produce fish-kills have been observed. The effect that most often produces a fish-kill is an oxygen slump. However, since similar oxygen slumps occurred in both treated and control plots at Lake Minnetonka (Petty et al, 1998 and Getsinger et al, 2000), it was believed that they were due to normal phenolgical variations due to seasonal changes.

Chronic risk quotients of <1.0 for triclopyr predict the chronic safety of these herbicides to fish. However, chronic risk quotients of >1.0 for our most sensitive invertebrate indicates that this segment of the biota is potentially at risk from exposure to triclopyr.

Furthermore, while chronic risk quotients of <1.0 for triclopyr, generally predict chronic safety to fish when they are in the water column, accurate prediction of chronic safety or lack of safety for aquatic invertebrates from exposure to treated sediment is not possible without an understanding of bioavailability factors that could mitigate the toxic effects of triclopyr sorbed to sediment. These factors could include maximum binding capacity of the sediment, bioavailability and likelihood of degradation on particular sediment types. However, since the concentration factor of triclopyr on sediment is less than one and the BCF on freshwater clams and crayfish is typically less than 2.0, it is unlikely that sediment species will be adversely impacted by sediment exposure from triclopyr.

The assumptions of risk analysis contain specific safety factors discussed by Urban and Cook (1986). The model discussed by Urban and Cook has been used since 1975 and was designed to provide a safety factor that would allow for differential variability and sensitivity among fish and wildlife species.

It was assumed that the slope of the dose response curve for the effects of a pesticide on most fish and wildlife species would be unknown. Since it is impossible to test every non-target-species that might be exposed, the following factors influence whether a correct risk management decision will be made:

1) Does the model predict risk so that the biota will be protected? Statistical analysis of the effects of slope on estimating the acute LC_{50} indicates that an expected

environmental concentration (EEC) value 10-times less than the acute LC_{50} would lead to 0.01% to 4% mortality.

2) Terrestrial organisms are believed to be less susceptible to environmental assault than aquatic species. Therefore, a less stringent EEC is used to designate unacceptable risk in these species. The less stringent EEC is 5-times less than the acute LC_{50} or LD_{50}, which would lead to a field mortality of approximately 10%, is used as a level of unacceptable risk in birds and mammals. The higher safety factors (listed in item 1) are believed to be necessary since aquatic organisms are less likely to be able to limit their exposure through behavioral modifications such as moving out of the treated area or switching to an alternative food source.

3) Larger safety factors are warranted for the protection of threatened and endangered species where a factor of 10-fold is insufficient to protect that segment of the biota. E.g., in cases where no mortality is acceptable, an EEC of 20 times less than the acute LC_{50} should be sufficient to ensure protection of species in which even a single death is of special concern.

4) For chronic effects, an EEC equal to the maximum allowable toxic concentration (MATC) or no observed effect concentration (NOEC) is believed to be sufficient to reduce risk to a minimum level, since statistical analysis indicates that if the EEC is less than the MATC or NOEC there is a 95% probability that no adverse impact to long-term survival, growth or reproduction will occur.

5) The above precautions will adequately protect any species acutely exposed to residues 10-fold lower than the EEC. However, to protect the entire biota or a segment of the biota, the acute EEC must be 10-fold lower than the LC_{50} and the chronic EEC must be less than the chronic MATC of the most sensitive species that you wish to protect.

The above criteria are considered rough estimates of potential risk to non-target organisms. The model used for ecological risk assessment does not provide a mechanism for estimating absolute uncertainty or an unchangeable probability of safety to the biota.

If the tested species are representative of the biota and are sufficient in number, uncertainty can be reduced to a minimum. Triclopyr herbicide is ranked as being slightly toxic to practically non-toxic to environmentally relevant fish and invertebrate species. For our database, the arthropod crustaceans have LC_{50}s that are similar for all species tested (>103 ppm a.e. for red swamp crayfish to 376 ppm a.e. for *Daphnia magna*). Since arthropod crustaceans are so similar in their response, it would be important in the future to test a variety of non-crustacean invertebrates as well as other environmentally relevant bivalves and crustaceans that are known to be sensitive to herbicides. However, triclopyr TEA has been tested with only 8 species of fish and 6 species of invertebrates. Such a relatively small database does not provide the confidence that the much larger endothall, 2,4-D and diquat databases provide. When a database is small, risk assessment and risk management decisions will be less certain and less adequate for protection of the more sensitive species in the biota. Many of the tested species of invertebrate are estuarine or marine such as *Palaemonetes pugio*, *Penaeus durorarum* and *Uca pugilator*. However, since estuarine and marine species are often more sensitive than their freshwater equivalents, additional sensitivity may be added to the risk assessment through their inclusion. Nevertheless, a greater number of freshwater invertebrate species need to be tested to improve the confidence in the risk assessment, since triclopyr is more likely to have significant impact in freshwater than in marine or estuarine environments.

Observations of fish or invertebrate kills due to the effects of triclopyr or other herbicides have been rare. Most cases of fish or invertebrate kills have been due to anaerobiasis caused by rotting, dead and dying vegetation (Frank, 1972). Treating only a portion of the water body at one time may reduce fish and invertebrate kills. This allows fish to avoid the lethal effects of anoxia by moving out of areas where the dissolved oxygen content is low.

The Expected Environmental Concentrations (EEC), as presented in Section 4.3.2.5 (Risk Analysis in Aquatic Species), are believed to be fairly accurate based on many years of successful risk management.

The fact that triclopyr appears to cause adverse impact to only 17% of the invertebrate species and none of the fish species indicates that the small number of species that may be adversely impacted may be substituted in the food web by species of similar size and nutritional quality. Field studies on the effects triclopyr TEA on the frequency and diversity of invertebrate taxa indicate that this assumption is true (Petty et al, 1998; Gardner and Grue, 1996 and Foster et al, 1997). Mitigating factors that are inherent to the nature of triclopyr TEA, like high solubility, low octanol/water partition coefficient and low sediment binding must be considered in order to make a risk assessment that is of value to the user. Also, the possibility of making an incorrect risk management decision must be weighed carefully if limited field data is available. Triclopyr TEA has only been used for the control of submerged, emerged and wetland associated weeds for only a few years. Further results from the practical use of Renovate® and Garlon® 3A, will allow for a more complete determination of the efficacy and safety of these products.

4.6 ADDITIONAL INFORMATION NEEDS

Summary: It is apparent that triclopyr acid and triclopyr TEA will not sorb significantly to sediment (Woodward et al, 1988). However, it is still conjectured that in-fauna and sediment associated organisms will be less affected when sediment is present than when it is absent (Green et al, 1989). Studies with sediment-free and sediment-amended test systems are necessary to prove or disprove this hypothesis.

The toxicity of triclopyr to sensitive fish and invertebrate species is well enough understood to adequately manage the risk associated with aquatic weed control. However, further investigations need to be conducted to determine what levels of triclopyr are safe to sensitive, threatened and endangered species (particularly salmon and sea-run trout). Additional studies emphasizing species indigenous to the Northwest should be conducted so that risk due to exposure can be managed more effectively. This is of particular concern for benthic organisms.

4.6.1 Soil and Sediment

The concentrations of triclopyr in sediment after application for the control of weeds have been adequately investigated. Triclopyr does not bind extensively to soil and sediment. The soil/water adsorption coefficient is less than 1.0 L/Kg on four different soil types. Therefore, adsorption is unlikely to be significant in removing triclopyr from the water column. Although the half-life (DT50 = 142 to 1,300 days) of triclopyr is very long in laboratory aerobic and anaerobic aquatic systems, it is not clear how rapidly triclopyr may be removed in the field if a significant population of microbes capable of degrading triclopyr are present. It is unclear if contaminated systems are more effective than pristine ones in removing triclopyr from an aquatic ecosystem. However, the rate of triclopyr removal from the water column is very short (DT50 <1 day) at Banks Lake (WA), Pend Oreille River (WA) and Lake Seminole (GA) but may be long (DT50 = 3.0 to 7.5 days) at Lake Seminole (GA), Lake Minnetonka (MN) and in ponds in California, Missouri and Texas. Triclopyr TEA is known to have high solubility (440 ppm a.e.) for the acid, high mobility (Kd = 0.165 to 0.975), slow field dissipation (DT50 = >4 days) and extensive leaching in field situations. Because of these physical properties, triclopyr TEA and TCP are likely to have adverse impact on surface and ground water. Since triclopyr is readily converted to TCP, TCP may also pose a risk to surface and ground water. Three hundred seventy-nine wells have been sampled for triclopyr. Five detections of triclopyr residues in ground water were reported in two states. All detections were very low (the maximum concentration reported was 0.00058 ppm). Triclopyr is currently not regulated under the Safe Drinking Water Act (SDWA). EPA's Office of Water has not established a maximum contaminant level (MCL) or a Drinking Water Lifetime Health Advisory (HAL) for triclopyr in drinking water. However, the proposed MCL is 0.5 ppm a.e. and the HAL has been estimated to be 0.350 ppm. Public water supply systems are not required to sample and analyze for triclopyr. Although EPA does not currently have surface or ground water advisories on triclopyr, surface and ground water studies may be necessary to determine the potential for triclopyr to leach under its new aquatic use labeling (EPA RED, 1998; Getsinger et al, 1997; Green et al, 1989; Getsinger et al, 2000; Petty et al, 1998 and Petty et al 1998).

The concentration of triclopyr in sediment has not been found to exceed ~0.3 ppm c.e. when applied at typical maximum use rates (Petty, 1998). Triclopyr is generally short lived in sediment with concentrations falling below a level of concern (0.1 ppm a.e.) within a few days to a few weeks. Since the potential for sorption is not great and sediment dissipation is fairly rapid, most sediment organisms will not be affected by the presence of triclopyr TEA. Sediment dwelling organisms have not been adversely impacted by triclopyr when exposed under field conditions (Petty et al, 1998; Gardner and Grue, 1996 and Green et al, 1989).

With the current knowledge of the concentration of triclopyr that typically occurs in sediment and a fairly good understanding of the toxicity of triclopyr to sediment organisms, risk can probably be managed effectively to protect them from the toxic effects of triclopyr. Several species of free swimming and sediment invertebrates have been tested with triclopyr TEA, and only one (eastern oyster) has been potentially impacted by concentrations that may be encountered in the environment. Environmental exposure concentrations are still many times less than the 48- to 96-hour EC_{50}s for triclopyr TEA. Eighty-three percent of tested invertebrate species are not affected by triclopyr TEA. Since triclopyr does not appear to affect any of the tested organisms of great importance in the food web, it will probably not be disrupted by the proper use of triclopyr. Other species of similar size and nutritional value should be able to substitute for those that may be temporarily lost from the water column due to treatment with triclopyr for aquatic weed control. The effects of triclopyr on the invertebrate biota and the dependency of fish on it are discussed extensively in section 4.3.2.

4.6.2 Water

The effects of water quality on the toxicity of triclopyr products has been adequately investigated. It has been demonstrated that triclopyr TEA products are unlikely to cause a change in water quality that will adversely impact the aquatic animals or non-target native plants species (Petty et al, 1998; Getsinger et al, 1997 and Getsinger et al, 2000). However, diel changes in dissolved oxygen content may impact survivability of fish (Petty et al, 1998). No significant impact was seen on nutrient levels or light transmission in treated ponds. Light transmission and dissolved oxygen content have been observed to increase with elimination of pest plant species prior to the establishment of thick stands of native aquatic plants (Petty et al, 1998). Frank (1972) has observed that the main problem causing water quality deterioration in treated water bodies is due to slumps in dissolved oxygen content due to the decay of treated vegetation. These oxygen slumps often lead to fish- and invertebrate- kills. Algal blooms have been observed to occur after treatment with triclopyr. However, it is unclear if this is due to nutrient release or normal phenological changes that occur during the treatment and growing season (Petty et al, 1998).

4.6.3 Plants

The evidence for algal and macrophyte blooms due to the release of nutrient nitrogen and phosphorous after treatment with triclopyr is unclear. Although green algae and diatoms were seen to bloom after treatment with triclopyr TEA, it is unclear whether this was due to a nutrient release or normal phenological changes in light and temperature that occur as the seasons change (Petty et al, 1998). To determine how triclopyr effects the water quality it would be necessary to conduct further mesocosm or field studies with triclopyr.

The planting of desirable vegetation in the aquatic environment after treatment with triclopyr has yet to receive serious investigation. However, many species of native plants including rushes (*Scirpus* spp.), cattails (*Typha* spp.), coontail (*Ceratophyllum* spp.), naiads (*Najas* spp.), various pondweed species (*Potamogeton* spp.), duckweed species (*Lemna* spp.), American waterweed (*Elodea canadensis*), water stargrass (*Heteranthera dubia*) and *Chara* spp. are largely unaffected in field situations (Gardner and Grue, 1996; Netherland and Getsinger, 1993; Wooodburn et al, 1993; Getsinger et al, 1997 and Petty et al, 1998). In the laboratory, the only species of macrophyte that have shown tolerance of triclopyr are *Lemna gibba* and *Lemna minor*. A number of algal species, particularly green algae and diatoms, are also tolerant of triclopyr TEA (Peterson et al, 1994) (Tables 13, 14, 15 and 16). After the native plant species have become established, the primary target species (*Myriophyllum spicatum*) may be suppressed in growth for several years due to effective competition from native plant species (Getsinger et al, 1997 and Netherland and Getsinger, 1993).

Frank (1972) has noted that post-treatment plantings of native non-noxious and non-invasive plants could increase diversity and decrease the numbers of the less desirable plants through competition. This would improve the habitat since a more diverse plant community would attract a more diverse animal community. The practicality and utility of post-treatment plantings of native plants and when they are best used should be evaluated on a case-by-case basis.

4.6.4 Acute and Chronic Animal Studies

Very few well-designed chronic toxicity studies have been conducted with triclopyr products. For an ideal understanding of chronic effects, early life-stage (ELS) studies may need to be conducted. Since Coho and Chinook salmon are so important in the Northwest, ELS studies may need to be conducted with these species. To have a better understanding of the chronic effects of triclopyr products on invertebrates, life-cycle studies may need to be conducted. The EPA RED (1998) has requested that the main toxic metabolite (TCP) be tested in an early life stage study with rainbow trout or chum or Coho salmon.

Ideally, additional acute and chronic work needs to be done on fully aquatic and water associated animal species. These species include aquatic reptiles (turtles), amphibians (salamanders, toads, and frogs), and lepidoptera and other insects associated with wetland communities or used as biocontrol agents on aquatic plants.

Great concern has recently been expressed concerning the effects of pesticides on benthic (sediment) organisms. In light of the potential impact of triclopyr on bivalves, additional testing needs to be conducted to determine the extent of the toxicity caused by triclopyr in both acute and chronic tests. The few studies conducted in the field indicate that most benthic invertebrate species are not affected directly by triclopyr. Some of the more sensitive species of estuarine and freshwater shrimp may need to be investigated for the effects of triclopyr against them in field situations. Other species of crustacean invertebrates need to be tested in both the laboratory and field situations since they have been shown to be susceptible to other herbicides. These include *Gammarus lacustris*, *Gammarus fasciatus*, *Hyallela azteca*, and grass shrimp (*Palaemoretes kadiakensis*), which appear to be important pray organisms for both fish that are commercially and recreationally important. Species which are resistant to triclopyr in the laboratory and field situations may be used as negative controls. For example, if an unexpected response occurs with these species, then there may be problems with the test design or there may be other factors which are influencing survival of the test organism.

4.7 MITIGATION MEASURES

*Summary: The use of triclopyr may be considered a mitigation measure when Eurasian watermilfoil (*Myriophyllum spicatum*), alligatorweed (*Alteranthera philoxeroides*), waterhyacinth (*Eichhornia crassipes*) parrotfeather (*Myriophyllum aquaticum*), pennywort (*Hydrocotyle *spp.) water lilies (*Nymphaea odorata *or* Nuphar *spp.) or waterprimrose (*Ludwigia uruguayensis*) are present. Reduction of these species may improve habitat for the growth of preferred plants, fish, zooplankton and benthic organisms. However, the main species indicated in the literature as being primary candidates for control by triclopyr TEA include* Myriophyllum spicatum *and* Lythrum salicaria.

Methods to lower levels of released phosphates during post-treatment aquatic plant decay could be useful. Although chelating agents such as fly ash metal, ferric iron, aluminum and zirconium have been used to remove phosphate from eutrophic lakes, there may be some risk to the aquatic environment due to the toxicity of these compounds to fish and invertebrates. In addition, by the time excessive phosphate levels are noticed, it may be too late to prevent an algal or heterotrophic bacterial bloom.

Mitigation for removal of excessive levels of triclopyr that have been released into the water due to an accident have not been significantly investigated. However, the development of such mitigation methods should be encouraged since accidents do happen occasionally.

The use of triclopyr itself may be considered a mitigation measure when floating emerged and/or submerged aquatic macrophytes are out of control. Treatment with appropriate concentrations of triclopyr may improve habitat for fish, pelagic aquatic invertebrates (zooplankton) and benthic organisms (catfish, common carp and sediment dwelling macro-invertebrates).

However, treatment with triclopyr may produce side effects that need to be mitigated. For example, release of too much phosphate due to the decay of treated plants or removal of phosphate during the development of aerobic conditions in a fairly shallow hypolimnion. When anaerobic conditions redevelop, phosphate and iron may be released once again and provide nutrients for growth, particularly after a sediment disturbance such as mechanical weed removal or a fall overturn. In order for these releases from the hypolimnion to be useful to photosynthetic organisms, the water must be both shallow and transparent enough for photosynthesis to occur. Removal of excess phosphate may be achieved by the addition of ferric iron, metals in fly ash, or salts of aluminum or zirconium. However, these remediation techniques may have an adverse impact on sensitive aquatic animals. Therefore, the negative impact of excess phosphate must be weighed against the possible negative affects of these chelating metals on the resident biota. This method is occasionally used to remove phosphate from eutrophic lakes and it could be used as a remedial measure when high phosphate levels are noticed due to the decay of herbicide treated aquatic plants. However, by the time high phosphate levels are noticed, it may already be too late to prevent algal or heterotrophic bacterial blooms (Goldman and Horne, 1983).

Levels of triclopyr that need remediation are unlikely to occur except in cases where there has been a spill. For example, if a treatment boat sinks, concentrations near the boat will be high enough to cause extensive fish-kill. For fish that have been studied (rainbow trout), there is no evidence that they can avoid triclopyr that is below toxic concentrations (LC_{50} = 400 ppm formulation equivalence = 144 ppm a.e.) (Morgan et al, 1991). In fact, rainbow trout only avoid triclopyr TEA at concentrations of 800 ppm formulation equivalence (288 ppm a.e.) which is high enough to cause immediate harm to exposed fish.

When triclopyr products are being used for control of aquatic weeds, the lowest effective concentration should be used. Triclopyr TEA has been effective in controlling weeds in aquaria and mesocosms (hydraulic channels) at concentrations ranging from 0.25 to 2.5 ppm a.e. However, longer exposure times are necessary when lower rates are used. Therefore, treatment at the lower concentrations may not be effective in field situations where extensive water flow (advection) or dispersion occurs. Nevertheless, these lower rates may be effective in ponds, lakes and coves where little or no water inflow or outflow occurs (Netherland and Getsinger, 1993 and proposed Garlon® 3A label). The use of this herbicide in open waterways where a lot of lateral mixing and dilution occur will also decrease the dissipation time (Ritter and Peacock, 2000).

It is conjectured that in cases where sediment or water becomes seriously contaminated, rates of dissipation may be improved by adding sediment containing high levels of microbes that may degrade triclopyr. This is currently just an unproven hypothesis that needs to be further investigated for its usefulness and practicality. However, this method has proven useful in some cases with other herbicides like endothall or 2,4-D. It is also conjectured that the addition of plants tolerant to triclopyr may assist in the removal of triclopyr from the waterway by direct adsorption. Getsinger et al (2000) has indicated that while pest species of plants may bioaccumulate triclopyr, non-target species like flatstem pondweed were not effective in adsorbing triclopyr from the water column. However, no experimental evidence exists to prove the efficacy of this approach. The use of chemostats or biofilms containing species of bacteria that may degrade triclopyr also has potential for mitigating cases of triclopyr water pollution. However, while it is conjectured that many of the species that degrade 2,4-D will also degrade triclopyr, this is only a hypothesis and no experimental evidence exists to support the use of chemostats and biofilms to remove triclopyr from water.

4.8 SUMMARY AND CONCLUSIONS

*Summary: In general, triclopyr TEA does not appear to adversely affect tested fish species. This lack of effect appears to extend to both acute and long term exposure. However, since only one species (*Pimephales promelas*) was tested for early life-stage effects, conclusions on the chronic effects of triclopyr TEA against fish must be considered tentative (Tables 2, 17, 19 and 21). The acute toxicity of triclopyr TEA on fish ranges from 82 ppm a.e. for rainbow trout to 176 ppm a.e. for fathead minnow. Fish tested at several exposure times had similar 24-, 48-, 72- and 96-hour* LC_{50} *values. The chronic toxicity for the only species tested in a 31-day early life stage study yielded an* LC_{50} *of between 52 to 81 ppm a.e. and NOEC, MATC and LOEC values of 33, 41 and 52 ppm, respectively. Since acute tests with the same batch of fathead minnows yielded a 96-hour* LC_{50} *of 82 ppm a.e., triclopyr TEA appears to be of similar toxicity after either acute or chronic exposure. Since there is a lack of chronicity, the EEC used to estimate risk is equal to the initial exposure after treating submerged (2.5 ppm a.e.), emerged (6.0 lbs a.e./acre = 4.4 ppm) or riparian wetland weeds (9 lbs a.e./acre = 6.6 ppm a.e.). The last two treatment scenarios assume that in a worst case situation that triclopyr TEA will be over-sprayed on a water body that is only 6 inches deep. In a water body that is 6 feet deep, the initial or peak concentration of triclopyr TEA used at 6.0 lbs a.e./acre 9.0 lbs a.e./acre is estimated to be 0.185 to 0.37 ppm or 0.27 ppm to 0.55 ppm a.e., respectively. When the EEC is compared to the acute* LC_{50} *in fish, it is noted that the risk quotient does not exceed the short term low level of concern (0.1);* $RQ = EEC/LC_{50} = 0.080 = 6.6$ *ppm a.e./82 ppm a.e. for rainbow trout present when wetland weeds are being controlled. When the EEC is compared to the predicted chronic MATC for rainbow trout, the risk quotient does not exceed the long-term level of concern (1.0); RQ = EEC/MATC = 0.24 = 6.6 ppm a.e/27 ppm a.e. Therefore, it is unlikely that fish populations exposed to the maximum use rate of triclopyr TEA will be acutely or chronically impacted and therefore, the fish biota is not considered to be at risk from acute or chronic exposure to triclopyr TEA.*

The crustacean component of the invertebrate biota does not appear to be susceptible to the adverse impact of triclopyr TEA. In the laboratory, the acute EC_{50} *of triclopyr TEA ranges from >103 ppm a.e. on red swamp crayfish to 376 ppm a.e. for* Daphnia magna *treated with a formulation that is similar to the current Garlon® 3A and Renovate® formulations (Tables 2, 18, 20 and 21). The acute risk quotient for these crustacean species is <0.1 which is lower than the low level of concern for protection of this segment biota;* $RQ = EEC/EC_{50} = <0.064 = 6.6$ *ppm a.e./103 ppm a.e. Invertebrate crustacean* *biota that are chronically exposed to triclopyr TEA are also unlikely to be at risk as indicated by the predicted or empirical laboratory risk quotients for red swamp (predicted Chronic RQ = <0.26 to <0.69) and* Daphnia magna *(empirical Chronic RQ = 0.071to 0 0.18). Since the chronic risk quotient does not exceed the level of concern (1.0), the invertebrate crustacean segment of the biota is not considered to be at risk from chronic exposure to triclopyr TEA.*

*However, one species of estuarine bivalve (*Crassostrea virginica*) may be at risk from exposure to triclopyr TEA. Since the* EC_{50} *for this species ranges from 22 to 41 ppm a.e., the acute risk quotient for this "most sensitive" species can range from 0.061 to 0.3. Since the acute risk quotient exceeds the low level of concern (0.1), this bivalve segment of the estuarine biota is considered to be at risk from acute exposure to triclopyr TEA. Nevertheless, because this risk quotient does not exceed the high level of concern (0.5), the effects of triclopyr TEA can be mitigated if it is registered and used as a restricted use formulation. Therefore, the estuarine bivalve sediment biota and other species with similar susceptibility should be considered to be not at significant risk from the acute exposure to triclopyr TEA if the product is used as a restricted use formulation. However, this segment of the biota and other similarly susceptible species may be at chronic risk since the predicted chronic MATC (2.1 ppm a.e.) is lower than the higher treatment rates for initial EECs (2.5, 4.4 and 6.6 ppm a.e.) and even lower than the 21-day TWA-EEC (1.1, 1.9 and 2.9 ppm) for the highest treatment rate. Mitigating factors that are likely to prevent exposure of estuarine species to triclopyr TEA include advection, dispersion and tidal flow and the fact that the proposed label does not allow for treatment of estuaries with triclopyr TEA. Furthermore, although an over spray with the 9.0 lb a.e./acre (6.6 ppm a.e.) treatment is possible, it is unlikely when a skilled operator is conducting the herbicide treatments. Also the EPA RED (1998) contends that chronic effects due to the over-spray of a shallow water body is not applicable to real world situations and only an over-spray or leaching into deep water (6 feet) is likely to have significant long-term impact. However, since the concentration due to a deep water over-spray or leaching of 6.0 to 9.0 lbs a.e. is more than 10-fold lower than the EEC (0.185 to 0.37 and 0.27 to 0.55 ppm a.e.), adverse impact to aquatic invertebrates or fish is extremely unlikely.*

The results from both fish and invertebrate laboratory studies have been verified in the field for acute exposures up to 2.5 ppm a.e. No significant short-term adverse impact has been noted on various game and non-game species from aquatic weed control practices (Petty et al, 1998; Houtman, 1997; Gardner and Grue, 1996; Green et al, 1989 and Green and Westerdahl, 1984). Also, no significant short-term impact has been noted on the most common invertebrate taxa found in the water column and in the sediment. Although unlikely, fish-kills may occur due to asphyxiation if an oxygen slump occurs. Water quality (dissolved oxygen content, conductivity, transparency -- light transmittance, conductivity and pH) generally appear to be largely unaffected by treatment with triclopyr TEA. However, dissolved oxygen content and light transmittance increase after the elimination of watermilfoil but return to normal levels after native aquatic species have established themselves. Long-term effects from 21 to 84 days also do not appear to affect fish (numbers) or invertebrate survival, reproduction or diversity (frequency of most common taxa).

Although triclopyr adversely impacts the invertebrate biota, 83% of invertebrate species tested will probably not be affected when it is used according to label instructions. Affects on bivalves and crayfish may be reduced when these species live in a normal *habitat and can dig into the sediment and become in-faunal organisms (Green et al, 1989). Fish food organisms appear to be unaffected by triclopyr TEA treatment. Therefore, it appears unlikely that fish will suffer adverse impact from nutritional deficits.*

Fish species and 83% of the tested invertebrate species should survive the whole pond treatments or spot treatments in lakes at concentrations up to 2.5 ppm a.e. However, not all species of algae and macrophytes are likely to survive treatment of a water body at concentrations of 0.25 to 2.5 ppm a.e. Treatment of water at 2.5 ppm a.e. with triclopyr TEA may cause moderate to high risk in blue-green algae, green algae, diatoms and aquatic macrophytes as indicated by laboratory results (Tables 13,14 and 16). However, field studies indicate that while target species like Myriophyllum spicatum *and* Lythrum salicaria *may be adversely impacted, native species such as* Scirpus *spp,* Typha *spp.* Ceratophyllum *spp.* Najas guadalupensis, N. minor, Potamogeton nodosus, P. crispus, P. zosteriformis, Elodea canadensis, Herteranthera dubia, Paspalum flutans *and* Chara *spp. may be tolerant (Netherland and Getsinger, 1993 and Getsinger et al, 1997). The tolerance of many native plants to the effects of triclopyr TEA in riverine, river cove and pond situations has been well documented. However, some species like* Ceratophyllum *spp.,* Najas guadalupnesis*, and* Elodea canadensis *may be adversely impacted in ponds where little or no inflow or outflow of treated water occurs. Although treated ponds maintained a healthy, diverse and numerous algal population, blue-green algae were generally reduced in numbers in treated ponds while green algae and diatoms were not adversely impacted by triclopyr treatment (Petty et al, 1998).*

Modeling studies indicate that the concentration of triclopyr TEA will not be high enough to adversely impact aquatic plants and algae if the treatment rate is not higher than 2.5 ppm a.e. and the setback distance is 200 to 2,000 feet (Ritter and Peacock, 2000). The exact distance of this setback varies with treatment rate and number of acres treated. If these setback distances are observed, the concentrations of triclopyr TEA in sensitive aquatic areas should be less than 0.5 ppm a.e., which is lower than the EC_{50} *for any aquatic macrophyte or algae tested. Therefore, if treatments are applied at a sufficient distance from areas containing sensitive aquatic vegetation, the plant and algal biota should not be at risk from the application of triclopyr TEA at labeled rates.*

*Available data also indicate that triclopyr TEA should not have adverse impact on amphibians (*Rana *spp.) even though the related triclopyr BEE (Garlon® 4) appears to be toxic to tadpoles at concentrations as low as 2.4 to 4.8 ppm a.i. However, since the toxicity of triclopyr BEE was similar in fish and amphibians, it is thought that triclopyr TEA will also be similarly toxic in fish and amphibians and therefore, unlikely to adversely impact larval amphibians (Berril et al, 1994). Although very little field data is available on the toxicity of triclopyr TEA to adult and larval amphibians, adults and tadpoles of* Rana pipiens *were common in test ponds eleven weeks after treatment of a pond in Columbia, Missouri with 2.5 ppm a.e. (Petty et al, 1998).*

The risk to aquatic life from the use of triclopyr was assessed using two methodologies. One of the methods was designed to compare chemicals for toxicity and the other was to determine whether or not the chemical was safe to the biota.

The first method is the U.S. EPA ecotoxicological risk categories for mammals, birds, and aquatic organisms (Table 1). For fish, birds and mammals, these categories are very highly toxic, moderately toxic, slightly toxic, and practically non-toxic. The exact quantitative values vary considerably depending on species and exposure route (EPA, 1982, and Brooks, 1973 in Ebasco, 1993) (Table 1). This method classifies triclopyr TEA as slightly toxic (LC_{50} = >10 to 100 ppm) to practically non-toxic (LC_{50} = > 100 ppm) for all species of fish and aquatic invertebrates. This indicates that, compared to other pesticide chemicals, the acute toxicity of triclopyr TEA is extremely low. The most sensitive species and stage of fish and invertebrate are rainbow trout fry and eastern oyster embryo/larvae with LC_{50}/EC_{50}s of 82 and ~22 ppm a.e., respectively (Tables 2, and 17 to 21). The conclusion of slight toxicity is verified by field studies. There have been no credible reports of fish- or invertebrate-kills due to the direct action of triclopyr TEA in the field. Frank (1972) reports that it is unusual for registered aquatic herbicides like triclopyr, 2,4-D, endothall or dichlobenil to cause fish-kills by direct toxic action but it is more usual when fish-kills are due to the secondary effect of anaerobiosis.

The second method assumes that for the test substance to be considered safe to the biota (Urban and Cook, 1986), the acute LC_{50} must be at least 10 times greater than the 4-day time weighed expected environmental concentration (TWA-EEC). However, since the toxicity of triclopyr appears to be similar in fish exposed for 24, 48, 72 or 96 hours, a TWA-EEC seemed inappropriate and the expected initial EECs for treatment of submerged (2.5 ppm) a.e., emerged (6.0 lbs a.e./acre = 4.4. ppm a.e.) and wetland species (9.0 lbs a.e./acre = 6.6 ppm a.e.) was used instead. For threatened and endangered species, the acute LC_{50} should be 20 times greater than the EEC for the test substance to be considered safe. The chronic NOEC or MATC must also be equal to, or greater than, the 28-day weighted EEC. However, since the toxicity of Triclopyr TEA at 96 hours (LC_{50} = 82 ppm a.e.) and 31 days (LC_{50} 52 to 81 ppm a.e.) were similar on fat-head minnow, the use of the TWA-EEC seemed inappropriate and the initial EECs were used instead. The US EPA RED (1998) for triclopyr is currently using the MATC to determine this level of concern.

Risk assessments indicate that triclopyr is acutely and chronically safe to the fish biota. The acute 96-hour LC_{50} for the most sensitive species in this segment of the biota is 82 ppm a.e. (Tables 2, 16, 18 and 20) and the EEC is 2.5, 4.4 and 6.6 ppm, depending on the treatment scenario. Therefore, the risk quotient will be less than the level of concern (0.1) for protection of this segment of the biota (RQ = 0.03 to 0.080). Triclopyr TEA also has a low chronic toxicity with predicted or empirical chronic toxicity ranging from 27 to 61 ppm c.e. for rainbow trout and Chinook salmon, respectively (Table 20). However, since the short-term risk assessment for endangered salmon species is sometimes higher than the level of concern (0.05), it would be unwise to use this product when salmon species are in the process of mating, breeding or smolting. The use of triclopyr TEA at other times should not adversely impact endangered salmon species. However, triclopyr TEA should not have an impact on endangered salmon species under any treatment scenario since the EEC is 15- to 73-fold lower than the LC_{50} on these sensitive species. There is no potential for adverse impact on salmon (RQ 0.013 to 0.025) when triclopyr is being used to control submerged weeds and no potential for adverse impact on salmon (RQ = 0.024 to 0.044) when triclopyr TEA is being used for control of emerged weeds. However, if a direct over-spray of shallow water with triclopyr TEA in the process of controlling wetland weeds occurs, there may be an adverse impact on salmon (RQ = 0.0360 to 0.067). However, in deeper water (6-feet deep) the initial exposure concentrations will be much lower (2.5, 0.185 to 0.367 and 0.270 to 0.55 ppm a.e., respectively) and adverse impact on salmon species is not likely (RQ = <0.0057 to 0.026).

The ECOFRAM approach would indicate that triclopyr TEA should not adversely impact any species of fish since the EEC concentrations (2.5 to 6.6 ppm a.e.) are less than the LC_{50} (>82 ppm a.e.) for the most sensitive species (rainbow trout). In the EPA RED (1998), where salmon species were not evaluated, the acute risk to fish was found to be acceptable at EEC concentrations as high as 6.6 ppm a.e. (RQ = <0.05). However, it is believed that some misinterpretation of the data may have occurred because many of the LC_{50} values were reported in a.i. equivalence when the original data reported the LC_{50} values in formulation equivalence. Such an error would lead to an approximately 2.5-fold error in the LC_{50} and in the final risk quotient value.

However, chronic risk assessment with the most sensitive fish species yields an RQ of <1.0 in all cases which is below the chronic level of concern (1.0). The predicted RQ for the most sensitive species is 0.092 to 0.24 which is considerably below the level of concern. Therefore, the fish biota should not be at risk for growth and reproductive effects.

Field-tests with triclopyr, generally support the conclusion that the use of triclopyr to control aquatic weeds does not harm fish. Both (caged) sentinel fish and fish caught by electro-fishing were not affected in numbers and a great diversity of game and non-game fish were typically seen in lakes and ponds (Petty et al, 1998; Houtman et al, 1997; Green et al, 1989 and Getsinger and Westerdahl, 1984). Although these studies were carried out for 21 to 84 days, it could not be determined if fish were impacted in their growth or reproduction. Petty et al (1998) found that adults and tadpoles of *Rana pipien*s were common in all test ponds from pretreatment to 11 weeks post treatment.

Risk assessments indicate that triclopyr TEA is acutely and chronically safe to the invertebrate crustacean species, but may not be safe for estuarine bivalves. The 96-hour LC_{50} for the most sensitive species of invertebrate crustacean is >103 ppm a.e. (Tables 2, 17, 19 and 20) and the 48-hour LC_{50} for embryo/larvae eastern oyster is ~22 ppm a.e. The risk quotient for aquatic crustaceans is less than the low level of concern (0.1) for the protection of this segment of the biota (RQ = <0.024 to <0.064). Triclopyr TEA should not have adverse impact for this segment of the biota (aquatic crustaceans). However, since the estuarine bivalve that was tested yielded an RQ that is greater than the low level of concern (RQ = 0.11 to 0.3), this segment of the biota may be at risk from the use of triclopyr TEA at concentrations between 2.5 an 6.6 ppm a.e. However, since the high level of concern is not exceeded (0.5), the registration and use of triclopyr TEA as a restricted use compound should prevent adverse impact.

Chronic risk assessments for aquatic crustaceans, indicates that growth and reproduction of this segment of the biota will not be adversely impacted. The chronic risk quotients for the most sensitive crustaceans is very low and does not exceed the chronic level of concern (RQ= <0.26 to <0.69). However, if a lack of chronicity is assumed, the chronic level of concern is exceeded by the estuarine bivalve (*Crassostrea virginica*) (RQ = 1.2 to 3.1). Therefore, growth and reproduction may be affected in this and other organisms of similar sensitivity. Mitigating this problem are label restrictions that prohibit triclopyr TEA from being applied to estuaries and the fact that triclopyr TEA will be extensively diluted by advection, dispersion and tidal flow. Modeling work indicates that in a linear distance of 2,000 feet or less, the concentration of triclopyr should have dissipated to 0.5 ppm a.e., which will produce acute and chronic risk quotients that are less than the levels of concern; acute RQ = EEC/LC_{50} = 0.023 = 0.5 ppm a.e./22 ppm a.e.; chronic RQ = EEC/MATC = 0.23 = 0.5 ppm a.e./2.1 ppm a.e. (Ritter and Peacock, 2000). While these model values assume an application rate of 2.5 ppm a.e., the risk quotient generated from a 6.6 ppm a.e. application would only be proportionately higher at 0.061 and 0.61 for the acute RQ and chronic RQ, respectively. These risk quotients generated for short-term and long-term conditions indicate that exposure to triclopyr TEA is unlikely to cause adverse impact to the standard invertebrate biota. Since sensitive, threatened or endangered estuarine invertebrate species have not been tested with triclopyr TEA, it would be improper to guess as to the safety of triclopyr towards these species. However, the risk quotient for the most sensitive standard environmentally relevant species is just slightly over the level of concern (0.05) for threatened and endangered species. Therefore, it seems unlikely that threatened and endangered species will be affected by the use of triclopyr TEA at labeled use rates.

It is the contention of the risk assessors using the ECOFRAM approach that this methodology is excessively sensitive. Risk assessors using the ECOFRAM approach believe that if the acute RQ for the most sensitive 10% of the species tested is less than 1.0 using reasonable estimates of a typical EEC, that the risk is minimal and the biota should not be at acute risk from the applied pesticide. Since the most sensitive environmentally relevant species of fish and invertebrate have LC_{50}s that are >3-fold lower than the highest initial EEC, triclopyr TEA should not acutely impact aquatic species according to the ECOFRAM approach.

In the Pend Oreille River (WA) and Moses Lake (WA) treated for the control of Eurasian watermilfoil and purple loosestrife, respectively, the maximum concentration of triclopyr TEA found in these water bodies was low immediately after treatment (~3 and 0.833 ppm). As described above, the concentration of triclopyr would be less than 0.5 ppm 2,000 feet from the treatment site (Getsinger et al, 1997 and Gardner and Grue, 1996). With such rapid dissipation, the impact of triclopyr on aquatic organisms would be minimal.

Field data support the risk assessment conclusions for the invertebrate biota. Treatment with triclopyr at 2.5 ppm a.e. did not adversely impact the invertebrate biota. A large, healthy and diverse invertebrate biota was present 11 weeks after treatment. These numbers and diversity will provide the various size and age classes of fish with appropriate food to sustain a large number of game and non-game fish (Petty et al, 1998; Gardner and Grue, 1996 and Getsinger and Westerdahl, 1984).

Other potential adverse impacts of triclopyr include adverse respiratory, behavioral and biochemical impact on rainbow trout or Coho salmon. However, these effects did not occur at concentrations below 72 ppm a.e. (200 ppm formulation equivalence) and are therefore, unlikely to occur in the field. Avoidance of triclopyr TEA at 288 ppm a.e., erratic swimming and labored respiration at 72 ppm a.e. and increases in the plasma lactate concentrations at 72 ppm a.e. were seen. These effects were not believed to be of importance at concentrations that might typically be found in the environment (0.25 to 6.6 ppm a.e.).

Myriophyllum spicatum is controlled with 100% efficacy at concentrations ranging from 0.25 to 2.5 ppm in aquariums and in mesocosms (hydraulic channels). At lower concentrations, longer exposure periods are necessary to achieve control. However, in lakes where great advection and/or dispersion was seen, concentrations of 1.0 to 2.5 ppm a.e. triclopyr TEA provided only 40% to 60% or 60% to 70% control of *Myriophyllum spicatum*. In situations where advection and/or dispersion do not occur, up to 99%

control was obtained. Furthermore, reestablishment of *Myriophllum spicatum* did not occur for three years due to the development of a robust native species community that was able to compete effectively with *Myriophyllum spicatum*. The risk quotients for algae and macrophytes generated under the worst case scenarios described above were found to be potentially low to high (RQ = <0.1 to 1.0) at treatment a concentration of 2.5 ppm a.e., and moderate to very high (0.1 to >1.0) at concentrations of 4.4 to 6.6 ppm a.e. However, it is unlikely that the highest concentrations will be experienced since this involves the unlikely event of a direct over-spray to shallow water when wetland (semi-terrestrial) weeds are the target for control. With the exception of the blue-green algae and marine diatoms, the most typical initial EEC (2.5 ppm a.e.) will not adversely impact most non-target vegetation (Table 16). Green algae, fresh water diatoms and *Lemna* species will only be impacted at a moderate level (RQ = 0.1 to 0.5) when treated with 2.5 ppm a.e. for the control of submerged weeds. Mesocosm studies and field studies indicate that green algae and diatoms grow more readily in treated ponds than other algal forms (Petty et al, 1998) and many of the native macrophytes described above will continue to grow after treatment at 0.25 to 2.5 ppm a.e. (Petty et al, 1998 and Netherland and Getsinger, 1993, and Getsinger et al, 1997). Furthermore, since the concentration of triclopyr TEA after treatment at 2.5 ppm falls below 0.5 ppm a.e. if the setback distances in the proposed label are observed, it is unlikely that triclopyr TEA will adversely impact aquatic vegetation that is located a significant distance (>2000 feet) from the treatment area.

In conclusion, triclopyr is safe to use for control of nuisance aquatic vegetation at labeled use rates and provides a large safety factor for protection of fish. The lower usage rates for control of submerged weeds (2.5 ppm), emerged weeds (6.0 lbs a.e./acre = 4.4 ppm a.e.) will not impact the standard fish species or the tested endangered *Oncorhyhchus* salmon species. Although the highest usage rate (9.0 lbs a.e./acre = 6.6 ppm a.e.) will not adversely affect the standard fish species, it may adversely impact endangered *Oncorhynchus* salmon species. However, this assumed the unusual situation where treatments used to control wetland species (9.0 lbs a.e./acre) are accidentally over-sprayed into shallow water (6.0-inches) deep. Direct over-spray or leaching of this treatment into deeper water (6-feet deep) is not likely to adversely impact the standard fish species or *Oncorhynchus* salmon species.

Only estuarine bivalves like *Crassostrea virginica* and similarly sensitive invertebrates are likely to be at risk from standard treatments (2.5, 4.4. or 6.6 ppm a.e.) with triclopyr TEA. These adverse impacts extend to both acute and chronic exposures. However, mitigating factors are that triclopyr TEA may not be applied to estuaries according to the label.
Furthermore, advection, dispersion and tidal flow make it unlikely that concentrations of greater than 0.5 to 1.32 ppm are likely to occur beyond the setback distances specified in the label. At these concentrations the acute and chronic risk quotients are unlikely to exceed the acute and chronic level of concern (0.1 and 1.0, respectively). Aquatic crustaceans are not at acute or chronic risk from exposure to triclopyr since the levels of concern are not exceeded under any treatment scenario.

Data from field studies tends to support the risk assessment. The effects of triclopyr TEA do not directly impact both game and non-game species of fish. Water quality is generally unaffected by the labeled use of triclopyr. Typically, the major taxa of invertebrate species found in the water column or sediment are not affected as to frequency or dominance and shifts in numbers (frequency) or dominant species is

usually correlated with changes in water temperature during the course of the treatment and growing season and not the direct impact of triclopyr TEA.

Use of triclopyr at labeled use rates is likely to adversely impact non-target species of algae and aquatic plants only when water impounds with little or no inflow or outflow are treated. In those cases, higher treatment rates (2.5 ppm a.e.) may adversely impact the more sensitive species (blue-green algae, and more sensitive non-target native species like coontail, southern naiads and American waterweed). Other species such as green algae, freshwater diatoms, *Potamogeton* spp., some species of naiad, water crowsfoot, water stargrass, water paspalum, rushes and cattails appear to be unaffected by the use of triclopyr at concentrations ranging from 0.25 to 2.5 ppm a.e. The lowest feasible rate should be used to control Eurasian water milfoil, alligatorweed, waterhyacinth, purple loosestrife, parrotfeather or other submerged, emerged or wetland weed in order to preserve the native plant species and allow them to compete effectively against the exotic noxious species. Non-target species of algae and aquatic plants will probably be unaffected if they are located 200 to 2,000 feet from the treatment site with the exact setback distance determined by the rate of treatment and the size of the area treated.

Garlon® 3A and Renovate® may be used at application rates up to 2.5 ppm a.e. for the control of submerged aquatic weeds, 6.0 lbs a.e./acre for the control of emerged aquatic weeds and 9.0 lbs a.e./acre for the control of other wetland weed species. Although use of triclopyr TEA for control of submerged and emerged weeds is unlikely to harm most fish species including endangered *Oncorhynchus* salmon species, use of 9.0 lbs a.e./acre to control other wetland weeds may adversely impact endangered fish if it is over-sprayed on to shallow water (6.0-inches deep); over-spraying or leaching into deeper water (6-feet deep) is unlikely to cause adverse impact on any fish species. Although all aquatic crustacean species are unaffected by triclopyr TEA applied according to label specifications, estuarine bivalves and similarly susceptible species may be affected by concentrations (2.5 ppm a.e.) of triclopyr TEA typically used to control submerged aquatic weeds. However, if the label is followed, triclopyr concentrations should be dissipated to levels that will not affect these sensitive species by the time the treated water enters the estuary. As described above, triclopyr TEA is effective in controlling a large number of aquatic macrophytes, although some of the species specified on the label may not be controlled for the entire treatment season with one application. The primary targets for weed control by triclopyr TEA in the State of Washington are Eurasian watermilfoil and purple loosestrife. Nevertheless, a large number of other submerged, emerged and wetland weeds may be controlled by triclopyr TEA, including alligatorweed. American lotus, burdock, Canada thistle, chickory, curly dock, dandelion, bindweeds, frogbit, lambsquarter, parrotfeather, pennywort, plantain, ragweed, tansy ragwort, tropical sodaapple, vetch, waterhyacinth, water lilies, waterprimrose and wild lettuce. Field data indicated that use of triclopyr products designated for aquatic use is safe to fish and common taxa of invertebrates.

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LIST OF TABLES

Table 1: U.S. EPA Ecotoxicological Catagories[1] for Mammals, Birds and Aquatic Organisms

Acute Oral Toxicity in Mammals (mg/Kg body wt)	Toxicity in Birds		Acute Toxicity in Fish and Invertebrates mg/L test solution	Toxicity Ranking
	Acute Oral (mg/Kg body weight)	Dietary mg/Kg feed		
<10	<10	<50	<0.1	Very Highly Toxic
10-50	10-50	50-500	0.1-1.0	Highly Toxic
>50-100	>50-500	>50-1000	>1-10	Moderately Toxic
>500-2000	>500-2000	>1000-5000	>10-100	Slightly Toxic
>2000	>2000	>5000	>100	Practically Non-Toxic

[1] Elizabeth Zucker, 1985. Hazard Evaluation Division, Standard Evaluation Procedure, and Acute Toxicity Test for Freshwater Fish. PB86-129277. EPA-540/9-85-006

Table 2: Toxicity of Triclopyr TEA to Different Aquatic Species; and Sensitive Species and Stages Tested

Species Name	**Common Name**	**Test Type**	**Age of Organism**	**Test Duration**	**Test Chemicals – Triclopyr TEA LC$_{50}$ or EC$_{50}$ & (MATC) in ppm a.e.**			
					24-hour Acute (ppm a.e.)	**48-hour Acute (ppm a.e.)**	**96-hour Acute (ppm a.e.)**	**Chronic MATC (ppm a.e.) LC$_{50}$/EC$_{50}$ (ppm a.e.)**
Algae								
Anabaena flos-aquae	Blue-green algae pond scum	AAM[1] Static (32.3% a.e.)	Log -growth	7-days				EC$_{50}$ = 4.2
Ankistrodesmus spp.	Green algae	AAM[1] Static (Garlon® 3A®)	Log-growth	4-days				EC$_{50}$ = 496 Garlon® 3A
Selenastrum Capricornutum	Green algae	AAM[1] Static (32.3% a.e.)	Log-growth	5				EC$_{50}$ = 5.5-12.6 (8.3)[5]
Selenastrum Capricornutum	Green algae	AAM[1] Static (98.8% triclopyr acid)	Log-growth	5				EC$_{50}$ = 47
Navicula pelliculosa	Freshwater diatom	Si/AAM[2] Static (32.3% a.e.)	Log-growth	7				EC$_{50}$ = 17
Skeletonema costatum	Marine diatom	Si/ASW[3] (32.3% a.e.)	Log-growth	5				EC$_{50}$ = 3.6-3.9 (3.8)[5]
Lemna gibba	Duckweed	Hoaglands[4] (32.3% a.e.)	2-frond	7-days				EC$_{50}$ =16-29 (21)[5]

Table 2: Toxicity of Triclopyr TEA to Different Aquatic Species; and Sensitive Species and Stages Tested (continued)

Species Name	**Common Name**	**Test Type**	**Age of Organism**	**Test Duration**	**Test Chemicals – Triclopyr TEA LC_{50} or EC_{50} & (MATC) in ppm a.e.**			
					24-hour Acute (ppm a.e.)	**48-hour Acute (ppm a.e.)**	**96-hour Acute (ppm a.e.)**	*Chronic* **MATC (ppm a.e.) LC_{50}/EC_{50} (ppm a.e.)**
Lemna gibba	Duckweed	Hoaglands[4] (32.3% a.e.)	2-frond	14-days				EC_{50} = 6.5-10.4 (8.2)[5]
Lemna minor	Common duckweed (several strains)	Hoaglands[4] (32.3% a.e.)	NS[6]	7-days				EC_{50} = 16-23 (19)[5]
Lemna minor	Common duckweed (several strains)	Hoaglands[4] (32.3% a.e.)	NS[6]	14-days				EC_{50} =18.4-27.0 (22)[5]
Fish and Amphibians								
Species Name	**Common Name**	**Test Type**	**Age of Organism**	**Test Duration**	**Test Chemicals – Triclopyr TEA LC_{50} or EC_{50} & (MATC) in ppm a.e.**			
					24-hour Acute (ppm a.e.)	**48-hour Acute (ppm a.e.)**	**96-hour Acute (ppm a.e.)**	**Chronic MATC (ppm) LC_{50}/EC_{50} (ppm)**
Lepomis macrochirus	Bluegill sunfish	Flow-through acute (31.4% a.e.)	38mm; 1.003g	4-days	161	147	147	
Lepomis macrochirus	Bluegill sunfish	Static acute (46.4% a.e.)	27.7mm; 0.6g	4-days			413	

Table 2: Toxicity of Triclopyr TEA to Different Aquatic Species; and Sensitive Species and Stages Tested (continued)

Species Name	**Common Name**	**Test Type**	**Age of Organism**	**Test Duration**	**Test Chemicals – Triclopyr TEA LC_{50} or EC_{50} & (MATC) in ppm a.e.**			
					24-hour Acute (ppm a.e.)	**48-hour Acute (ppm a.e.)**	**96-hour Acute (ppm a.e.)**	**Chronic MATC (ppm a.e.) LC_{50}/EC_{50} (ppm a.e.)**
Menidea beryllina	Tidewater silverside	Flow-through acute (32.1% a.e.)	0.10g	4-days	109	109	93	
Oncorhychus mykiss	Rainbow trout	Flow-through & Static acute (32.8-36% a.e.)	40-53mm; 0.7-1.1g	4-days	126-165 (144)[5]	91-157 (120)[5]	82-128 (102)[5]	
Oncorhychus mykiss	Rainbow trout	Static acute (46.4% a.e.)	23.5mm; 0.24g	4-days			256	
Oncorhynchus keta	Chum salmon	Static acute (36% a.e.)	45mm;0.5g	4-days	114	104	96	
Oncorhynchus kisutch	Coho Salmon	Static acute (36% a.e.)	40mm; 0.5g	4-days	179	171	167	
Oncorhynchus nerka	Sockeye salmon	Static acute (36% a.e.)	39mm; 0.5g	4-days	127	112	112	
Oncorhynchus tshawytscha	Chinook salmon	Static acute (36% a.e. acute)	68mm, 2.7g	4-days	170	112	99	

Table 2: Toxicity of Triclopyr TEA to Different Aquatic Species; and Sensitive Species and Stages Tested (continued)

Species Name	Common Name	Test Type	Age of Organism	Test Duration	Test Chemicals – Triclopyr TEA LC_{50} or EC_{50} & (MATC) in ppm a.e.			
					24-hour Acute (ppm a.e.)	**48-hour Acute (ppm a.e.)**	**96-hour Acute (ppm a.e.)**	**Chronic MATC (ppm) LC_{50}/EC_{50} (ppm)**
Pimephales promelas	Fathead minnow	Flow-through acute (32.2% a.e.)	16mm; 0.22g	4-days			86	
Pimephales promelas	Fathead minnow	Static acute (32.2% a.e.)	16mm; 0.22g	4-days	184-233 (207)	184-233 (207)	176	
Pimephales promelas	Fathead minnow	Flow-through Chronic (32.2% a.e.)	Egg to free-swimming fry	31-days				MATC= 52 LC_{50} = 52-81 (65)[5]
Pimephales promelas	Fathead minnow	Flow-through Acute (46.4% a.e.)	31mm;0.54g	4-days			439	
Invertebrates								
Crassostrea virginica	Eastern oyster	SW[7] Acute 31.4% a.e.	Embryo/ larvae	2-days		>18-<27 (22)[5]		
Crassostrea virginica	Eastern oyster	SW[7] Flow-through 33.0% a.e.	Spats	4-days			41	
Daphnia magna	Water flea	Static Renewal Acute 32.2% a.e.	1st instar	2-days	376			

Table 2: Toxicity of Triclopyr TEA to Different Aquatic Species; and Sensitive Species and Stages Tested (continued)

Species Name	**Common Name**	**Test Type**	**Age of Organism**	**Test Duration**	**Test Chemicals – Triclopyr TEA LC_{50} or EC_{50} & (MATC) in ppm a.e.**			
					24-hour Acute (ppm a.e.)	**48-hour Acute (ppm a.e.)**	**96-hour Acute (ppm a.e.)**	**Chronic MATC (ppm) LC_{50}/EC_{50} (ppm)**
Daphnia magna	Water flea	SW[7] Static Acute 46.4% a.e.	1st instar	2-days	360			
Daphnia magna	Water flea	Static Renewal Chronic 32.2% ppm a.e.	21-days					MATC = 35 LC_{50} = 367
Palaemonetes pugio	Grass shrimp	SW[7] Flow-through Acute 33.0% a.e.	4-days	>377	>377		234	
Penaeus duroarum	Pink shrimp	SW[7] NS[6] acute 31.3% a.e.	4-days				281	
Uca pugilator	Fiddler crab	SW[7] NS[6] acute 31.4% a.e.	4-days				>314	
Procambarus clarki	Crayfish	NS[6] acute	NS				>103	

[1] AAM = Artificial algal medium (Miller et al, 1978 in Hughes, 1987).
[2] Si/AAM = Artificial algal medium fortified with silicate (Miller et al, 1978 in Hughes, 1987).
[3] Si/ASW = Artificial seawater medium fortified with silicate (Walsh and Alexander, 1980 in Cowgill and Milazzo, 1987).
[4] Hoaglands = Modified Hoaglands Solution (Cowgill et al, 1988).
[5] Geometric mean of range extremes
[6] NS = not specified
[7] SW = Seawater

Table 3: Soil Erodability Factors

Surface Layer Texture	Estimated K
Clay, Clay Loam, Loam, Silty Loam	0.32
Fine Sandy Loam, Loamy very Fine Sand, Sand Loam	0.24
Loamy Fine Sand, Loamy Sand	0.17
Sand	0.15
Silt Loam, Silty Clay Loam, Very Fine Sandy Loam	0.37

Source: Barfield et al., 1981in EBASCO, 1993 and USDA. 1978a in EBASCO, 1993

Table 4: Classification of Pesticides Based on Bioconcentration Factor

Classification	Bioaccumulation Factor[1]	Characteristics
Non-accumulative	≤10	Pesticide readily decreases when organism is removed from exposure
Slightly accumulative	60-700	Pesticide is only gradually lost when organism is removed from exposure or pesticide is degraded by organisms
Moderately Accumulative	700-8,000	Pesticide is only gradually lost when organism is removed from exposure, or pesticide is slowly degraded by organism
Highly accumulative	≥8,000	Pesticide is not lost when an organism is removed from exposure, or pesticide is not significantly degraded by organism

Source: Weber, 1977 in EBACO, 1993

[1] As defined by Weber, 1977 in EBACO, bioaccumulation = concentration in aquatic organism/ concentration in water. Typically, this is termed the bioconcentration factor and not the bioaccumulation factor which takes into account accumulation from all sources of exposure including food, water consumed, exposure water and if applicable, air exposure.

Table 5: Concentration of Triclopyr in Water, Hydrosoil and Fish for Triclopyr TEA Applied to Ponds in California, Missouri and Texas

Time after Application Days	Application Rate (ppm a.e.)	Water (ppm a.e.)	Hydrosoil (ppm a.e.)	Fish (ppm a.e.)	Concentration Factor Soil	Concentration Factor Fish
California Pond B T1/2 = 7.5 days for water; T= 3.6 days for hydrosoil						
0	2.5	2.29	0.68	0.024	0.29	0.13
1	2.5	2.08	0.68	0.019	0.32	0.15
2	2.5	2.08	NT[1]	NT[1]	NT[1]	NT[1]
3	2.5	2.02	0.58	<0.01	0.29	0.29
5	2.5	1.70	NT[1]	NT[1]	NT[1]	NT[1]
7	2.5	1.59	0.52	<0.01	0.32	<0.006
14	2.5	1.31	0.12	<0.01	0.091	<0.0076
21	2.5	0.64	0.039	<0.01	0.061	<0.015
28	2.5	0.19	<0.01	<0.01	<0.05	<0.052
42	2.5	0.0030	<0.01	NT[1]	NC[2]	NT[1]
84	2.5	0.0030	<0.01	NT[1]	NC[2]	NT[1]
Missouri Pond B T1/2 = 6.1 days for water and T1/2 = 3.2 days for hydrosoil						
0	2.5	1.91	0.021	0.026	0.011	0.014
1	2.5	2.35	0.08	0.014	0.034	0.0060
2	2.5	1.75	NT[1]	NT[1]	NT[1]	NT[1]
3	2.5	1.49	0.073	0.017	0.048	0.011
5	2.5	1.39	NT[1]	NT[1]	NT[1]	NT[1]
7	2.5	1.04	0.075	0.014	0.072	0.013
14	2.5	0.50	<0.01	<0.01	<0.02	<0.02
21	2.5	0.14	<0.01	<0.01	<0.07	<0.07
28	2.5	0.032	<0.01	<0.01	<0.31	<0.31
42	2.5	0.0040	<0.01	NT[1]	NC[2]	NT[1]
84	2.5	0.00030	<0.01	NT[1]	NC[2]	NT[1]
Texas Pond B T1/2 = 6.3 days for water; T1/2 = 4.6 days for sediment; T1/2 = 6.2 days for fish fillet						
Time after Application Days	**Application Rate (ppm a.e.)**	**Water (ppm a.e.)**	**Hydrosoil (ppm a.e.)**	**Fish (ppm a.e.)**	**Concentration Factor Soil**	**Concentration Factor Fish**
0	2.5	2.26	0.21	0.030	0.093	0.013
1	2.5	2.15	0.45	0.027	0.21	0.013
2	2.5	2.26	NT[1]	NT[1]	NT[1]	NT[1]
3	2.5	1.92	0.363	0.019	0.19	0.0099
5	2.5	1.62	NT[1]	NT[1]	NT[1]	NT[1]
7	2.5	1.33	0.32	<0.01	0.24	<0.0075
14	2.5	0.56	0.097	<0.01	0.17	<0.018
21	2.5	0.19	0.023	<0.01	0.12	<0.053
28	2.5	0.070	<0.01	<0.01	<0.14	<0.14
42	2.5	0.0063	<0.01	NT[1]	NC[2]	NT[1]
84	2.5	0.0017	<0.01	NT[1]	NC[2]	NT[1]

NT = sample not taken

NC = Value not calculated

Table 6: Dissolved Oxygen Concentration (ppm) at Different Temperatures

Temperature in Degrees Centigrade	Dissolved Oxygen Concentration in ppm
0	14.2
1	13.9
2	13.5
3	13.1
4	12.7
5	12.4
6	12.1
7	11.7
8	11.5
9	11.2
10	10.9
11	10.7
12	10.5
13	10.2
14	10.0
15	9.8
16	9.6
17	9.4
18	9.1
19	9.0
20	8.9
21	8.6
22	8.5
23	8.4
24	8.3
25	8.2

Table 7: Relationship of pH and Temperature to the Percentage of Unionized Ammonia [NH4OH + NH3 (dissolved)] in Freshwater

pH	Temperature (°C)				
	5°	10°	15°	20°	25°
6.5	0.04%	0.06%	0.09%	0.13%	0.18%
7.0	0.12%	0.19%	0.27%	0.40%	0.55%
7.5	0.39%	0.59%	0.85%	1.24%	1.73%
8.0	1.22%	1.83%	2.65%	3.83%	5.28%
8.5	3.77%	5.55%	7.98%	11.2%	15.0%
9.0	11.0%	15.7%	21.4%	28.5%	35.8%

Table 8: Toxicity of Adjuvants Registered for Aquatic Use to Aquatic Animals

Adjuvant	Use	Use Rate L/ha	Depth for LC_{50} to be Achieved	96 hr LC_{50} (mg/L)		
				Bluegill	**Rainbow Trout**	***Daphnia magna***
Spar-Mate®	Surfactant	140	1.5	0.96		
R-11®	Surfactant			4.2-5.5	3.8	19
X77®	Surfactant	4.7	0.1	4.3	4.2	2.0
Cide-Kick II®	Surfactant	7.0	0.1	4.3-5.2		
Widespread®	Surfactant			7.0	6.6	16
Induce®	Surfactant/ Accelerant			7.3	8.3	18
Super Spread 200®	Surfactant			9.3		
Liqua Wet®	Surfactant			11.0	13	7.2
Spreader Sticker®	Surfactant/ Sticker			35	36	48
Formula 403		18.7	0.1	37		
IVOD®		18.7	0.1	37		
Passage®				52	75	17
Big Sur®		4.7	<0.1	112		
Nalquatic®	Thickener	9.3	<0.1	200		
LI-700®				210	130	170
Agri Dex®	Surfactant/ Accelerant			>1,000	>1,000	>1,000
Polysar®	Thickener	4.7	<0.1	3,600		
Herbex®		2.3	<0.1	8,000		
Foamer®	Anti-Foam					
No Foam A®	Anti-Foam					
Dyne Amic®	Surfactant					
Penetrator®	Surfactant/ Accelerant					

Table 9: Plant Susceptibility to Triclopyr TEA

Plants and Algae– Killed by Application of Triclopyr TEA

Laboratory Results from Standard Plant Species Used for Evaluation of Triclopyr TEA (Table 2 and EPA RED, 1998):

Plant	EC_{50} (ppm a.e.)	EC_{50} (lbs a.e./acre in 6 inches of water)
Lemna gibba G3	6.5-10.4	8.8-14.1
Lemna minor (various strains)	18.4-27.0	25.0-36.7
Anabaena flos-aquae	4.2	5.7
Ankistrodesmus spp. (T82)	496	674
Navicula pelliculosa	15.3-17.0	20.8-23.1
Skeletonema costatum	3.8-4.8	5.2-6.5
Selenastrum capricornutum	5.5-12.6	7.5-17.1

Submerged Aquatic Plants Controlled in the Field (Garlon® 3A Proposed Label)

Plant	Recommended use rate (ppm a.e.)	Notes
Myriophyllum spicatum	0.75 to 2.5 ppm	Higher rates may be necessary in areas of greater water exchange. These areas my require repeat applications.
Myriophylum aquaticum	0.75 to 2.5 ppm	
Hydrocotyle *spp.*	0.75 to 2.5 ppm	

Floating and Emerged Aquatic Plants Controlled at Maximum Field use Rate (Garlon® 3A Proposed Label)

Plant or Algae	Recommended use rate (lbs a.e./acre)	Notes
Floating Plants		
Eichhornia crassipes	1.5-6.0 lbs a.e./acre	Thoroughly wet foliage with spray mixture. Use a non-ionic surfactant. Repeat treatment may be necessary to control re-growth.
Emerged Plants		
Alternanthera philoxreoides	2.25 to 6.0 lbs a.e./acre	Thoroughly wet foliage with spray mixture, Use a non-ionic surfactant. Only emerged foliage of alligatorweed will be controlled. Repeat treatment may be necessary to control re-growth.
Nelumbo lutea	1.5-6.0 lbs a.e./acre	
Nymphae odorata	1.5-6.0 lbs a.e./acre	
Nuphar *spp.*	1.5-6.0 lbs a.e./acre	

Table 9: Plant Susceptibility to Triclopyr TEA(Continued)

Wetland Associated species (Proposed Garlon® 3A Label):

Terrestrial Annual and Perennial Broadleaf Weeds

Plant	Recommended use rate (lbs a.e./acre)	
Annual and Perennial Herbaceous Broadleaf Weeds		
Convolvulus spp.	1.0 to 6 lbs a.e./acre	*Surfactants should be used. Thickening agents may be used to prevent drift. Leaves should be thoroughly wetted by the spray solution.*
Arctium minus	1.0 to 6 lbs a.e./acre	
Circium arvense	1.0 to 6 lbs a.e./acre	
Rumex crispus	1.0 to 6 lbs a.e./acre	
Taraxacum officinale	1.0 to 6 lbs a.e./acre	
Convolvulus arvensis	1.0 to 6 lbs a.e./acre	
Plantago spp.	1.0 to 6 lbs a.e./acre	
Lythrum salicaria	1.0 to 6 lbs a.e./acre	
Ambrosia spp.	1.0 to 6 lbs a.e./acre	
Senecio joacobea	1.0 to 6 lbs a.e./acre	
Solanum aculeastum	1.0 to 6 lbs a.e./acre	
Viscia spp.	1.0 to 6 lbs a.e./acre	
Lactuca spp.		
Woody brush plants	6.0-9.0 lbs a.e./acre	Surfactants should be used. Thickening agents may be used to prevent drift. Leaves should be thoroughly wetted by the spray solution.

Crop Plant Susceptibility to Triclopyr TEA (EPA RED, 1998)

Crop Plant	EC25 (lbs a.e./acre) or (ppm a.e.)
Seed Germination	
Sugar beets	0.0005 ppm a.e.
Corn	0.0083 ppm a.e.
Seedling Emergence	
Corn	>0.24 lbs a.e./acre
Radish	>0.72 lbs a.e./acre
Vegetative Vigor	
Onion	0.12 lbs a.e./acre
Sunflower	0.005 lbs a.e./acre

Table 10: Acute to Chronic Ratio for Triclopyr TEA on Aquatic Organisms

Species	Length of Chronic Test	Triclopyr Formulation	Acute Toxicity (LC_{50} ppm a.e)	Chronic Toxicity MATC[1] (ppm a.e.)	Ratio[2]	References
Fathead minnow	Egg to free-swimming fry	Triclopyr TEA 32.2% ppm a.e.	86-176 (123)[3]	41	2.1-4.3 (3.0)[3]	Mayes et al, 1983; Mayes et al, 1984
Daphnia magna	Life-cycle	Triclopyr TEA 32.2% ppm a.e.	376	35	10.7	Gersich et al, 1982; Gersich et al, 1984)

[1] Chronic Values are MATC (maximum allowable toxic concentration) values unless otherwise noted.

[2] Geometric mean and of all pertinent data = 5.7 (2.3 to 13.9) where item in parenthesis is the range based on $10^{(\text{Mean-st.dev})}$ to $10^{(\text{Mean+ St.dev.})}$.

[3] Values in parenthesis are geometric means of all valid individual values.

Table 11: Acute Toxicity of Triclopyr TEA to Algae and Aquatic Macrophytes

Species	Test Media	End Point	Length of Test (days)	%A.I. %A.E.	EC$_{50}$ (ppm formulation)	EC$_{50}$ (ppm a.i.)	EC$_{50}$ (ppm a.e.)	Source
Lemna gibba (Duckweed)	Hoaglands^{2}	Frond count and Plant count	14	45.0 a.i. 32.3 a.e.	19.9-20.1 (19.9)^{6}	(9.0-9.1 (9.0)^{6}	6.4-6.5 (6.5)^{6}	Cowgill et al, 1987
Lemna gibba (Common duckweed)	Hoaglands^{2}	1	7	45.0 a.i. 32.3 a.e.	48-90 (65)	22-41 (29)	16-29 (21)	Cowgill et al, 1988
Lemna minor (Common duckweed)	Hoaglands^{2}	1	14	45.0 a.i. 32.3 a.e.	24-57 (27)	11-39 (14)	7.8-18 (10.4)	Cowgill et al, 1988
Lemna minor (Common duckweed)	Hoaglands^{2}	1	7	45.0 a.i. 32.3 a.e.			16-23 (19)	Cowgill et al, 1988
Lemna minor (Common duckweed)	Hoaglands^{2}	1	14	45.0 a.i. 32.3 a.e.			18.4-27 (23)	Cowgill et al, 1988
Anabaena flos-aquae (Filamentous N-Fixing Blue-green algae)	AAM^{3}	Cell count	7	45.0 a.i. 32.3 a.e.	13.3	5.97	4.2	Hughes, 1987
Ankistrodesmus spp. (Green algae)	AAM^{3}	Cell count	4	Garlon® 3A	N/A	692	496	Gardner et al, 1997
Selenastrum capricornutum (Green algae)	AAM^{3}	Cell count & Cell volume	5	45.0 a.i. 32.3 a.e.	16.7-17-6 (17.1)	7.6-7.9 (7.7)	5.4-5.7 (5.5)	Cowgill & Milazo, 1989
Selenastrum capricornutum (Green algae)	AAM^{3}	Cell count & Cell volume	5	45.0 a.i. 32.3 a.e.	39.6	17.6	12.6	Dill & Milazzo, 1987
Selenastrum capricornutum (Green algae)	AAM^{3}	Cell count & Cell volume	5	98.8 Technical triclopyr acid	45-50 (47)	44-49 (47)	44-49 (47)	Cowgill and Milazo, 1989

Table 11: Acute Toxicity of Triclopyr TEA to Algae and Aquatic Macrophytes (Continued)

Species	Test Media	End Point	Length of Test (days)	%A.I. %A.E.	EC_{50} (ppm formulation)	EC_{50} (ppm a.i.)	EC_{50} (ppm a.e.)	Source
Navicula pelliculosa (Chrysophyte = diatom)	Si/AAM[4]	Cell count	7	45.0 a.i. 32.3 a.e.	53	24	17	Hughes, 1987
Skeletonema costatum (Marine diatom)	Si/ASW[5]	Cell count & Cell volume	5	45.0 a.i. 32.3 a.e.	11.1-12.3 (11.7)	5.0-5.5 (5.3)	3.6-3.9 (3.8)	Cowgill & Milazzo, 1987, Cowgill et al, 1989

[1] End point is frond count, plant count; biomass, chlorophyll a concentration, chlorophyll b concentration.
[2] Hoaglands = Hoagland's solution (as described in Cowgill and Milazzo, 1987).
[3] AAM = Artificial algal medium (Miller et al 1978 in Hughes, 1987).
[4] Si/AAM = Silicate fortified Artificial algal medium (Miller et al ,1978 in Hughes, 1987).
[5] Si/ASW = Silicate fortified Artificial Seawater (Walsh and Alexander, 1980 in Cowgill and Milazzo, 1987).
[6] Geometric mean of all relevant data.

Table 12: Potential Hazard Ratios[1] of Triclopyr TEA for Eleven Species of Non-Target Aquatic Green Algae, Blue-Green Algae and Duckweed (Peterson et al, 1994)

Peterson'sHazard Rating[1] and Percent Inhibition of Growth when Exposed to an EEC of 2.57 ppm a.e. of Triclopyr TEA			
	High	**Moderate**	**Potentially low**
Lemna minor (Duckweed)	23(4)[2]*		
Green Algae			
Cyclotella meneghiana			-15(12)[3]
Nitzschia sp.,F110-D			-4(3)
Scenedesmus quadricauda, F11		13(9)	
Selenastrum capricornutum, U1648			-24(6)
Blue-Green Algae			
Microcystis aeruginosa, PCC7820			-10(8)
Microcystis aeruginosa, U2063			-2(12)
Oscillatoria sp.,T129			-9(3)
Pseudoanabaena, F63		13(3)*	
Anabaena inaequalis, U381			-4(13)
Aphanizomenon flos-aquae, F107			-34(16)*

[1] Peterson's Hazard Ratings: Very High if EEC causes >50% reduction in growth and RQ = >1.0; High if EEC causes 25 to 50% reduction in growth and RQ is much greater than 0.1 (0.5 to <1.0); Moderate if EEC causes 5 to 25% reduction in growth and RQ = >0.1 (>0.1 to <0.5); Potentially Low if EEC causes <5% reduction in growth and RQ = <0.1.

[2] Values in parenthesis are standard deviations.

[3] Negative values indicate a stimulation in growth.

* Statistically different from the controls.

Table 13: Laboratory Effects of Triclopyr Formulations on Macrophytes and phytoplankton

Results	References[1]
Selenastrum capricornutum is stimulated to fix CO_2 at concentrations of triclopyr of 2.56 ppm a.e.	Peterson et al, 1994
Aphanizomenon flos-aquae is stimulated to fix CO_2 at concentrations of triclopyr TEA at 2.56 ppm a.e.	Peterson at al, 1994
Duckweed (*Lemna minor*) is inhibited in growth by concentrations of triclopyr TEA at 2.56 ppm a.e.	Peterson et al, 1994
Cyclotella meneghiana, Nitzshcia sp., *Scenedesmus quadricuada*, *Microcystis aeruginosa, Oscillatoria* sp. and *Anabaena inaequalis* are unaffected in their CO_2 fixation capacity at concentrations of triclopyr TEA at 2.56 ppm a.e.	Peterson et al, 1994
Pseudoanabaena spp. is inhibited in its CO_2 capacity at concentrations of triclopyr TEA at 2.56 ppm a.e.	Peterson et al, 1994
Direct over-spray of triclopyr TEA at rates of 9 lbs a.e./acre (6.6 ppm a.e.) may adversely impact *Lemna gibba, Anabaena flos-aquae, Selenastrum capricornutum* and *Skeletonema costatum*.	EPA RED, 1998
Direct over-spray of Triclopyr TEA at rates of 6 lb a.e./acre (4.4 ppm a.e.) may adversely impact *Anabaena flos-aquae* and *Skeletonema costatum*.	EPA RED, 1998
Treatment of wetlands adjacent to a water body with triclopyr TEA at 6 lbs a.e./acre (0.185 to 0.37 ppm a.e.)[1] or 9 lbs a.e./acre (0.270 to 0.55 ppm a.e.)[1] will probably not impact standard aquatic plant and algae test species.	EPA RED, 1998
Direct treatment of a water body to control submerged aquatic weeds at concentrations to triclopyr TEA at 2.5 ppm a.e. will probably not impact standard aquatic plant and algae test species.	EPA RED, 1998

[1] Assumes a direct over-spray or leaching into 6 feet of water.

Table 14: Field-Effects of Triclopyr Products on Macrophytes and Phytoplankton

Results	References
Treatment of ponds at Elk Grove, CA with triclopyr at 2.5 ppm a.e. to control submerged aquatic macrophytes generally resulted in a decrease in blue-green algae and an increase in green algae and diatoms. However, a healthy and diverse phytoplankton community was maintained throughout the 12-week evaluation period.	Petty et al, 1998
Treatment of ponds at Columbia, MO with triclopyr at 2.5 ppm a.e. to control submerged aquatic macrophytes generally resulted in green algae dominated plant communities. However, it is unclear if this is a direct result of the affect of triclopyr TEA or due to a moderate relatively stable spring and summer maximum water temperature (25 to 30°C)	Petty et al, 1998
Treatment of ponds at Lewisville, TX with triclopyr at 2.5 ppm a.e. to control submerged aquatic macrophytes did not appear to directly impact the growth of the green algae *Spirogyra* and *Cladophora*. The growth of these species was triggered by increase in water temperature during the course of the study.	Petty et al, 1998
Treatment of Lake Minnetonka, MN with triclopyr TEA at 2.5 ppm a.e. resulted in the reduction of Eurasian watermilfoil and the growth of flatstem pondweed.	Foster et al, 1997
Treatment of ponds in Elk Grove, CA with triclopyr TEA at 2.5 ppm a.e. resulted in elimination of coontail (*Ceratophyllum demersum*) by 12 weeks after treatment.	Petty et al, 1998
Treatment of ponds in Columbia, MO with triclopyr TEA at 2.5 ppm a.e. did not appear to directly impact aquatic macrophytes and charophytes. Naiads remained abundant in both treated and untreated ponds. Decreases in charophyte numbers were probably due to normal phenological senescence and failure to compete effectively with naiad species.	Petty et al, 1998
Treatment of ponds in Lewisville, TX with triclopyr TEA at 2.5 ppm a.e. effectively controlled Eurasian watermilfoil. American waterweed and southern naiad decreased in treated ponds due to sensitivity to this high rate of triclopyr TEA treatment. Decreases in water paspalum were probably due to increasing water temperatures and not the direct effects of triclopyr TEA. Triclopyr TEA had no significant impact on *Chara* spp.	Petty et al, 1998
Purple loosestrife was controlled for one year in wetland areas near Moses Lake, Washington. However, 50% recovery of the purple loosestrife stands were seen by the end of the first year after treatment at 6% formulation equivalence of triclopyr TEA. This treatment did not adversely impact sentinel plants (*Lemna gibba*)	Gardner and Grue, 1996
Eurasian watermilfoil has been shown to be controlled at rates ranging up to 2.5 ppm a.e. in the Pend Oreille River, Washington, Lake Seminole, Georgia and the Guntersville Reservoir, Alabama.	McNabb, 1993; Getsinger et al, 1996, 1997 and Turner et al, 1995 in Houtman et al, 1997 and in Petty et al, 1998.

Table 15: Risk Assessment for Blue-green Algae, Green Algae, Diatoms and Macrophytes with Triclopyr TEA Products

Species Name	Test Chemical – Triclopyr TEA Products EC_{50} (ppm a.e.) & [Risk Quotient (RQ[1] = EEC[2]/EC_{50})] and {Risk Level }(Peterson et al, 1994)				
	Direct Over-spray 9.0 lbs a.e./acre Initial EEC = 6.6 ppm a.e.[3]	**Direct Over-spray 6.0 lbs a.e./acre Initial EEC = 4.4 ppm a.e.[4]**	**Aquatic application EEC = 2.5 ppm a.e.[5]**	**Wetlands Application 9.0 lb a.e./acre EEC = 0.270 ppm a.e.[6]**	**Wetlands application 6.0 lbs a.e./acre EEC= 0.185 ppm a.e.[7]**
Anabaena flos-aquae (Blue-green algae)	(4.2) [1.6] {Very high}	(4.2) [1.1] (Very high)	(4.2) (0.60) (High)	(4.2) [0.064] {Potentially low}	(4.2) [0.04] {Potentially low}
Anksitrodesmus spp. (T82 culture) (Green algae)	(496) [0.014] {Potentially low}	(496) [0.009] {Potentially low}	(496) [0.005] {Potentially low}	(496) [0.0005] {Potentially low}	(496) [0.0004] {Potentially low}
Selenastrum capricornutum (Green algae)	(5.5-12.6) [1.2 to 0.53] {Very high to High}	(5.5-12.6) [0.8-0.34] {High to Moderate}	(5.5-12.6) [0.45-0.20] {Moderate}	(5.5-12.6) [0.049-0.021] {Potentially low}	(5.5-12.6) [0.034 to 0.015) {Potentially low}
Navicula pelliculosa (Diatom)	(17) {0.39) {Moderate}	17 [0.25] {Moderate}	17 [0.15] {Moderate}	17 [0.015] {Potentially low}	17 [0.011] {Potentially Low}
Skeletonema costatum (Marine diatom)	(3.6-3.9) [1.8-1.7 {Very high}	(3.6-3.9) [1.2-1.1 {Very high}	(3.6-3.9) [0.70-0.64] {High}	(3.6-3.9) [0.075-0.069] {Potentially low}	(3.6-3.9) [0.051-0.047] {Potentially low}
Lemna gibba G3 (7-day test	(16-29) [0.41-0.23] {Moderate}	(16-29) [0.23-0.15] {Moderate}	(16-29) [0.16-0.086] {Moderate to {Potentially low}	(16-29) [0.017-0.0093] {Potentially low}	(16-29) [0.012-0.0064] {Potentially low}
Lemna gibba G3 (14-day test)	(6.5-10.4) [1.0-0.63] [Very high to High]	(6.5-10.4) [.68 to 0.42] {High to Moderate)	(6.5-10.4) [0.38-0.24] {Moderate}	(6.5-10.4) [0.041-0.026] {Potentially low}	(6.5-10.4) [0.028-0.018] {Potentially low}

Table 15: Risk Assessment for Blue-green Algae, Green Algae, Diatoms and Macrophytes with Triclopyr TEA Products (continued)

Species Name	**Test Chemical – Triclopyr TEA Products** **EC_{50} (ppm a.e.) & [Risk Quotient ($RQ^1 = EEC^2/EC_{50}$)] and {Risk Level }(Peterson et al, 1994)**				
	Direct Over-spray 9.0 lbs a.e./acre Initial EEC = 6.6 ppm a.e.[3]	**Direct Over-spray 6.0 lbs a.e./acre Initial EEC = 4.4 ppm a.e.[4]**	**Aquatic application EEC = 2.5 ppm a.e.[5]**	**Wetlands Application 9.0 lb a.e./acre EEC = 0.270 ppm a.e.[6]**	**Wetlands application 6.0 lbs a.e./acre EEC= 0.185 ppm a.e.[7]**
Lemna minor (Various strains) 7-day test (Common duckweed)	(16-23) [0.41-0.29] {Moderate}	(16-23) [0.28-0.19] {Moderate}	(16-23) [0.16-0.11] {Moderate}	(16-23) [0.016-0.011] {Potentially low}	(16-23) [0.012-0.0080] {Potentially low}
Lemna minor (Various strains) 14-day test (Common duckweed)	(18.4-27) [0.36-0.24] {Moderate}	(18.4-27) [0.24-0.16] {Moderate}	(18.4-27) [0.14-0.09] {Moderate to Potentially low}	(18.4-27) [0.014-0.07] {Potentially low}	(18.4-27) [0.010-0.0069] {Potentially low}

1 RQ = Risk Quotient (unitless).
2 EEC = Expected Environmental Concentration.
3 Highest EEC immediately after treatment with maximum labeled use rate for controlling non-aquatic wetland weed species assuming a direct over-spray to six inches of water = 9.0 lbs a.e./acre = 6.6 ppm a.e. (EPA RED, 1998).
4 Highest EEC immediately after treatment with highest labeled use rate for controlling floating, emergent or shore weed in a direct over-spray to a water body of six inches in depth containing no weeds and a depth of six inches = 6.0 lbs a.e./acre = 4.4 ppm a.e. (EPA RED, 1998).
5 Highest EEC immediately after application with maximum-labeled use rate for controlling submerged aquatic weeds is 2.5 ppm a.e.
6 Highest (peak) GENEEC (Generic expected environmental concentrations) after application with the maximum use rate to control non-aquatic wetland species = 9.0 lbs a.e./acre = 0.270 ppm (EPA RED, 1998).
7 Highest (peak) GENEEC after application with the maximum use rate to control non-aquatic wetland (shore) species = 6.0 lbs a.e./acre = 0.185 (EPA RED, 1998).

Table 16: Acute Toxicity of Triclopyr TEA Products to Fish

Species	Size/ Age Class	Test Conditions S/F[1], T[2],Hard[3]	%AI[4] or % AE[5]	1D LC$_{50}$ (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	2D LC$_{50}$ (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	3D LC$_{50}$ (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	4D LC$_{50}$ (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	Source
Lepomis macrochirus (Bluegill sunfish)	38mm; 1.003g	F;24;37	47.8 a.i.[4] 31.4 a.e.[5]	(512) [245] {161}	(471) [225] {147}	(471) [225] {147}	(471) [225] {147}	Batchelder, 1973
Lepomis macrochirus (Bluegill sunfish)	27.7mm;0.6g	S;22;100	64.7 a.i. 46.4 a.e.	N/A[9]	N/A[9]	N/A[9]	(891) [576] {413}	McCarty et al, 1978
Lepomis macrochirus (Bluegill sunfish)	38mm; 1.003g	F;24;37	triclopyr acid (technical)	{150.5}	{149}	{149}	{148}	Batchelder, 1973
Menidia beryllina (Tidewater silverside)	0.10g	F;21;SW 14-17 ppt	44.7 a.i. 32.07 a.e.	(>340) [>152] {>109}	(>340) [>152] {>109}	(>340) [>152] {>109}	(290) [130] {93}	Ward & Boeri, 1989
Onchorhynchus mykiss (Rainbow trout)	53mm; 1.1g	F;13;37	47.8 a.i. 34.3 a.e.	(366) [175] {126}	(265) [126] {91}	(249) [119] {85}	(240) [115] {82}	Batchelder, 1973
Onchorhynchus mykiss (Rainbow trout)	53mm; 1.1g	F;13;37	triclopyr acid (technical)	{120}	{119}	(117}	{117}	Batchelder, 1973
Onchorhynchus mykiss (Rainbow trout)	40mm	N/A[9];14;4.5	44.4 a.i. 32.8 a.e.	N/A[9]	N/A[9]	N/A[9]	(400) [178] {128}	Morgan et al, 1991
Onchorhynchus mykiss (Rainbow trout)	41mm; 0.7g	S;6,3.25-3.81	50.2 a.i. 36 a.e.	(457) [229] {165}	(435) [218] {157}	(420) [211] {151}	(420) [211] {151}	Wan et al, 1987
Onchorhynchus mykiss (Rainbow trout)	23.5mm; 0.24g	F;12;100	64.7 a.i. 46.4 a.e.	N/A[9]	N/A[9]	N/A[9]	(552) [357] {256}	McCarty et al, 1978

Table 16: Acute Toxicity of Triclopyr TEA Products to Fish (continued)

Species	Size/ Age Class	Test Conditions S/F[1], T[2],Hard[3]	%AI[4] or % AE[5]	1D LC$_{50}$ (ppm form)[6] [ppm a.i.] {ppm a.e.}[8]	2D LC$_{50}$ (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	3D LC$_{50}$ (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	4D LC$_{50}$ (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	Source
Oncorhynchus keta (Chum salmon)	45mm; 0.5g	S;6,3.25-3.81	50.2 a.i. 36 a.e.	(316) [159] {114}	(290) [146] {104}	(275) [138] {99}	(267) [134] {96}	Wan et al, 1987
Oncorhynchus kisutch (Coho salmon)	40mm; 0.5g	S;6,3.25-3.81	50.2 a.i. 36 a.e.	(498) [250] {179}	(476) [238] {171}	(476) [238] {171}	(463) [232] {167}	Wan et al, 1987
Oncorhynchus nerka (Sockeye salmon)	39mm; 0.5g	S;6,3.25-3.81	50.2 a.i. 36 a.e.	(353) [177] {127}	(311) [156] {112}	(311) [156] {112}	(311) [156] {112}	Wan et al, 1987
Oncorhynchus tshawytscha (Chinook salmon)	68mm; 2.7g	S;6,3.25-3.81	50.2 a.i. 36 a.e.	(472) [237] {170}	(312) [157] {112}	(283) [142] {102)	(275) [253] {99}	Wan et al, 1987
Pimephales promelas (Fathead minnow)	16-31mm; 0.22g	F;17;101-132	44.9 a.i. 32.2 a.e.	N/A[9]	N/A[9]	N/A[9]	(268) [120] {86}	Mayes et al, 1983; Mayes et al, 1984
Pimephales promelas (Fathead minnow)	16-31mm; 0.22g	S;17;101-132	44.9 a.i. 32.2 a.e.	(570-720) [256-323] {184-233}	(570-720) [256-323] {184-233}	(570-720) [256-323] {184-233}	(546) [245] {176}	Mayes et al, 1983; Mayes et al, 1984
Pimephales promelas (Fathead minnow)	31mm; 0.54g	F;12;100	64.7 a.i. 46.4 a.e.	N/A	N/A	N/A	(947) [613] {439}	McCarty et al, 1978

[1] S = Static; F = follow-through; SR = Static renewal.
[2] T = Temperature in °C
[3] Hardness in ppm $CaCO_3$
[4] %AI = percent active ingredient
[5] % AE = percent acid equivalence
[6] ppm form = ppm formulation equivalence
[7] ppm a.i. = ppm active ingredient ppm
ppm a.e. = ppm acid equivalence
[8] N/A = data not available

Table 17: Acute Toxicity of Triclopyr TEA Products to Invertebrates

Species	Size/Age Class	Test Conditions S/F[1], T[2],hard[3]	%AI[4] %AE[5]	Exposure Time (Hours)	1D EC_{50} (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	2D EC_{50} (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	3D EC_{50} (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	4D EC_{50} (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	Source
Crassostrea virginica (Eastern oyster)	Embryos & larvae	NS[9];20;SW	43.8 a.i. 31.4 a.e.	48	N/A[10]	(>56-<87) [>25-<38] {>18-<27)	N/A[10]	N/A[10]	Heitmuller , 1975
Crassostrea virginica (Eastern oyster)	Juvenile Shell deposition	F;22;SW 30 ppt	46.1 a.i. 33.0 a.e.	96	N/A[10]	N/A[10]	N/A[10]	(125) [58] {41}	Ward et al, 1993
Daphnia magna (Water flea)	<24 hr	SR,20,149	44.9 a.i. 32.2 a.e.	48	N/A[10]	(1170) [525] {376}	N/A[10]	N/A[10]	Gersich et al, 1982; Gersich et al, 1984
Daphnia magna (Water flea)	<24 hr	S;17;100	64.7 a.i. 46.4 a.e.	48	N/A[10]	(775) [501] {360}	N/A[10]	N/A[10]	McCarty et al, 1978
Daphnia magna (Water flea)	<24 hr	S;25;100	99.5 a.e. triclopyr acid equiv.	48	(203) [202] {202}	(133) [132] {132}	N/A[10]	N/A[10]	McCarty, 1977
Palaemonetes pugio (Grass Shrimp)	Probably <24hr	F;21;SW 17 ppt	46.1 a.i. 33.0 ppm a.e.	96	(>1141) [>526] {>377}	(1141) [>526] {>377}	(757) [349] {250}	(707) [326] {234}	Ward et al , 1992
Penaeus durorarum (Pink Shrimp)	Probably <24hr	NS15;SW 24 ppt	43.8 a.i. 31.4 a.e.	96	N/A[10]	N/A[10]	N/A[10]	(895) [392] {281}	Heitmuller P.T, 1975

Table 17: Acute Toxicity of Triclopyr TEA Products to Invertebrates (continued)

Species	Size/Age Class	Test Conditions S/F[1], T[2],hard[3]	%AI[4] %AE[5]	Exposure Time (Hours)	1D EC_{50} (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	2D EC_{50} (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	3D EC_{50} (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	4D EC_{50} (ppm form)[6] [ppm a.i.][7] {ppm a.e.}[8]	Source
Uca pugilator (Fiddler crab)	NR	NS;15;SW 20 ppt	43.8 a.i. 31.4 a.e.	96	N/A[10]	N/A[10]	N/A[10]	(>1000) [>438] {>314}	Heitmuller P.T, 1975
Procambarus clarki (Crayfish)	NR	NS;NS;NS	NR	96	N/A[10]	N/A[10]	N/A[10]	N/A[10] [>143] {>103}	Barron et al, 1991 in Woodburn et al, 1993

1 S = Static; F = flow-through; SR = Static renewal.
2 T = Temperature in °C
3 Hardness in ppm $CaCO_3$
4 %AI = percent active ingredient
5 % AE = percent acid equivalence
6 ppm form = ppm formulation equivalence
7 ppm a.i. = ppm active ingredient
8 ppm a.e. = ppm acid equivalence
9 NS = Not specified
10 N/A = data not available

Table 18: Chronic Toxicity of Triclopyr TEA Products to Fish

Species	Size/Age Class	Test Conditions S/F[1]; T[2]; hard[3]	%AI[4] % AE[5]	Test Duration (days)	NOEC[6] (ppm form)[9] [ppm a.i.][10] {ppm a.e.}[11]	MATC[7] (ppm form)[9] [ppm a.i.][10] {ppm a.e.}[11]	LOEC[8] (ppm form)[9] [ppm a.i.][10] {ppm a.e.}[11]	LC_{50} (ppm form)[9] [ppm a.i.][10] {ppm a.e.}[11]	Source
Pimephales promelas (Fathead minnow)	egg to fry	F;25;101-132	44.9 a.i. 32.2 a.e.	31	(104) [47] {33}	(130) [58] {41}	(162) [73] {52}	162-253 [73-114] {52-81}	Mayes et al; 1983, Mayes et al, 1984

[1] S = Static; F = follow-through; SR = Static renewal.
[2] T = Temperature in °C
[3] Hardness in ppm $CaCO_3$
[4] %AI = percent active ingredient
[5] % AE = percent acid equivalence
[6] NOEC = Statistical No Observed Effect Concentration.
[7] MATC = Maximum Acceptable Toxic Concentration = geometric meant of NOEC and LOEC.
[8] LOEC = Statistical Lowest Observed Effect Concentration
[9] ppm form = ppm formulation equivalence
[10] ppm a.i. = ppm active ingredient
[11] ppm a.e. = ppm acid equivalence

Table 19: Chronic Toxicity of Triclopyr TEA Products to Invertebrates (Daphnid)

Species	**Size/Age Class**	**Test Conditions S/F[1]; T[2]; hard[3]**	**%AI[4] % AE[5]**	**Test Duration (days)**	**NOEC[6] (ppm form)[9] [ppm a.i.][10] {ppm a.e.}[11]**	**MATC[7] (ppm form)[9] [ppm a.i.][10] {ppm a.e.}[11]**	**LOEC[8] (ppm form)[9] [ppm a.i.][10] {ppm a.e.}[11]**	**LC_{50} (ppm form)[9] [ppm a.i.][10] {ppm a.e.}[11]**	**Source**
Daphnia magna (Water flea)	<24 hr at start	SR,20,149	44.9 a.i. 32.2 a.e.	21	(80.7) [36] {26}	(110) [49] {35}	(149) [67] {48}	(1140) [512] {367}	Gersich, et al1982; Gersich et al 1984; Gersich et al 1985

[1] S = Static; F = follow-through; SR = Static renewal.
[2] T = Temperature in °C.
[3] Hardness in ppm $CaCO_3$.
[4] %AI = percent active ingredient.
[5] % AE = percent acid equivalence.
[6] NOEC = Statistical No Observed Effect Concentration.
[7] MATC = Maximum Acceptable Toxic Concentration = geometric meant of NOEC and LOEC.
[8] LOEC = Statistical Lowest Observed Effect Concentration.
[9] ppm form = ppm formulation equivalence.
[10] ppm a.i. = ppm active ingredient.
[11] ppm a.e. = ppm acid equivalence.

Table 20: Acute and Chronic Risk Assessment for Triclopyr TEA for Commercial Grade Product (44 to 50 % a.i.; 31 to 36 % a.e.)

Test Type	Exposure Time	Species	EEC[1] (ppm a.e.)	Acute LC_{50}[2] (ppm c.e.)	Chronic MATC[3] (ppm c.e.)	Risk Quotient [4]	Level of Concern[5]	RQ exceeds LOC[5]
Fish								
Acute	4-days	*Lepomis macrochirus* (Bluegill sunfish)	2.5[6]-6.6[7]	147		0.017-0.044	0.1[8]/0.5[9]	No/No
Acute	4-days	*Menidia beryllina* (Tidewater silverside)	2.5-6.6	93		0.027-0.071	0.1[8]/0.5[9]	No/No
Acute	4-days	*Oncorhynchus mykiss* (Rainbow trout)	2.5-6.6	82		0.030-0.080	0.1[8]/0.5[9]	No/No
Acute	4-days	*Oncorhynchus keta* (Chum salmon)	2.5-6.6	99		0.025-0.067	0.1[8]/0.5[9]	No/No
Acute	4-days	*Oncorhynchus kisutch* (Coho salmon)	2.5-6.6	167		0.015-0.040	0.1[8]/0.5[9]	No/No
Acute	4-days	*Oncorhynchus nerka* (Sockeye salmon)	2.5-6.6	112		0.022-0.059	0.1[8]/0.5[9]	No/No
Acute	4-days	*Oncorhynchus tshawytcha* (Chinook salmon)	2.5-6.6	182		0.013-0.036	0.1[8]/0.5[9]	No/No
Acute	4-days	*Pimepahles promelas* (Fathead minnow)	2.5-6.6	86		0.029-0.076	0.1[8]/0.5[9]	No/No
Chronic	31-days	*Lepomis macrochirus* (Bluegill sunfish)	2.5-6.6	147	49[10]	0.051-0.13	1.0	No
Chronic	31-days	*Oncorhynchus mykiss* (Rainbow trout)	2.5-6.6	82	27[10]	0.092-0.24	1.0	No
Chronic	31-days	*Oncorhynchus keta* (Chum salmon)	2.5-6.6	99	33[10]	0.76-0.20	1.0	No
Chronic	31-days	*Oncorhynchus kisutch* (Coho salmon)	2.5-6.6	167	56[10]	0.044-0.12	1.0	No
Chronic	31-days	*Oncorhynchus nerka* (Sockeye salmon)	2.5-6.6	112	37[10]	0.067-0.18	1.0	No

Table 20: Acute and Chronic Risk Assessment for Triclopyr TEA for Commercial Grade Product (44 to 50 % a.i.; 31 to 36 ppm a.e.) (continued)

Test Type	Exposure Time	Species	EEC[1] (ppm a.e.)	Acute LC_{50}[2] (ppm a.e.)	Chronic MATC[3] (ppm a.e.)	Risk Quotient [4]	Level of Concern[5]	RQ exceeds LOC[5]
Chronic	31-days	*Oncorhynchus tshawytcha* (Chinook salmon)	2.5-6.6	182	61[10]	0.041-0.11	1.0	No
Chronic	31-days	*Pimepahles promelas* (Fathead minnow)	2.5-6.6	86	41[11]	0.061-0.16	1.0	No
Invertebrates								
Acute	2-days	*Crassostrea virginica* (Embryo & larval oyster)	2.5-6.6	>18 to <27 (22)		0.11-0.3	0.1[8]/0.5[9]	Yes/No
Acute	2-days	*Crassostrea virginica* (Embryo & larval oyster)	2.1[12]-5.5[13]	>18 to <27 (22)		0.095-0.25	0.1[8]/0.5[9]	Yes/No
Acute	4-days	*Crassostrea virginica* (Oyster spats) 4-8mm	2.5-6.6	41		0.061 -0.16	0.1[8]/0.5[9]	Yes/No
Acute	4-days	*Crassostrea virginica* (Oyster spats)	2.1[12]-5.5[13]	41		0.051-0.13	0.1[8]/0.5[9]	Probably Not/No
Acute	2-days	*Daphnia magna* (1st instar water flea)	2.5-6.6	376		0.0.0066-0.018	0.1[8]/0.5[9]	No/No
Acute	4-days	*Palaemonetes pugio* (1st-instar grass shrimp)	2.5-6.6	234		0.011-0.028	0.1[8]/0.5[9]	No/No
Acute	4-days	Penaeus duroarum (1st-Instar Pink shrimp)	2.5-6.6	281		0.0089-0.023	0.1[8]/0.5[9]	No/No
Acute	4-days	*Uca pugiltor* (Fiddler crab)	2.5-6.6	>314		<0.0080-<0.021	0.1[8]/0.5[9]	No/No

Table 20: Acute and Chronic Risk Assessment for Triclopyr TEA for Commercial Grade Product (44 to 50 % a.i.; 31 to 36 ppm a.e.) (continued)

Test Type	Exposure Time	Species	EEC[1] (ppm a.e.)	Acute LC_{50}[2] (ppm a.e.)	Chronic MATC[3] (ppm a.e.)	Risk Quotient [4]	Level of Concern[5]	RQ exceeds LOC[5]
Acute	4-days	*Procambarus clarki* (Red swamp crayfish)	2.5-6.6	>103		<0.024-<0.064	0.1[8]/0.5[9]	No/No
Chronic	21days	*Crassostrea virginica* (Embryo & larval oyster)	2.5-6.6	>18 to <27 (22)	2.1[14]	1.2-3.1	1.0	Yes
Chronic	21-days	*Crassostrea virginica* (Embryo & larval oyster)	1.1[16]-2.9[17]	>18 to <27 (22)	2.1[14]	0.52-1.4	1.0	Yes at higher dosage
Chronic	21-days	*Crassostrea virginica* (Oyster spats) 4-8mm	2.5-6.6	41	3.8[14]	0.66-1.7	1.0	Yes at higher dosage
Chronic	21-days	*Crassostrea virginica* (Oyster spats)	1.1[16]-2.9[17]	41	3.8[14]	0.28-0.76	1.0	No
Chronic	21-days	*Daphnia magna* (1st instar water flea)	2.5-6.6	376	35[15]	0.071-0.18	1.0	No
Chronic	21-days	*Palaemonetes pugio* (1st-instar grass shrimp)	2.5-6.6	234	22[12]	0.10-0.30	1.0	No
Chronic	21-days	*Penaeus duroarum* (1st-Instar Pink shrimp)	2.5-6.6	281	26[12]	0.096-0.25	1.0	No
Chronic	21-days	*Uca pugiltor* (Fiddler crab)	2.5-6.6	>314	>29[12]	<0.086-<0.23	1.0	No
Chronic	21-days	*Procambarus clarki* (Red swamp crayfish)	2.5-6.6	>103	>9.6[12]	<0.26-<0.69	1.0	No

[1] EEC = Expected Environmental Concentration.

Table 20: Acute and Chronic Risk Assessment for Triclopyr TEA for Commercial Grade Product (44 to 50 % a.i.; 31 to 36 ppm a.e.) (continued)

[2] Acute LC_{50} = Concentration of Triclopyr that kills or immobilized 50% of the test animals in the exposure time.
[3] Predicted Chronic MATC = (acute LC_{50}/(acute/chronic toxicity ratio).
[4] RQ = Risk Quotient.
[5] LOC = Level of Concern = Value (EEC/toxicity) which should not be exceeded as an indicator of the safety of a particular pesticide application to the biota.
[6] EEC immediately after treatment at maximum treatment rate (2.5 ppm a.e.) for control of emersed aquatic weeds.
[7] EEC immediately after accidental direct over-spray of water during treatment of wetland species at 9 lbs a.e./acre in six inches of water (6.6 ppm a.e.).
[8] LOC of 0.1 is the low level of concern where adverse impact is not expected.
[9] LOC of 0.5 is the high level of concern where use of the compound as a restricted use pesticide is necessary to help prevent adverse impact.
[10] Predicted chronic MATC for fish = LC_{50}/3.0.
[11] Chronic MATC for fathead minnow is and empirical value.
[12] 4-day time weighted average EEC after treatment at maximum use rate (2.5 ppm a.e.) to control emersed aquatic weeds.
[13] 4-day time weighted average EEC after accidental over-spray of water during treatment of wetland terrestrial weeds at 9.0 lbs a.e./acre in six inches of water (6.6 ppm a.e.).
[14] Predicted chronic invertebrate MATC = LC50/10.7.
[15] Chronic MATC for *Daphnia magna* is an empirical value.
[16] 21-day time weighted average EEC after treatment at maximum use rate (2.5 ppm a.e.) to control emersed aquatic weeds.
[17] 21-day time weighted average EEC after accidental over-spray of water during treatment of wetland terrestrial weeds at 9.0 lbs a.e./acre in six inches of water (6.6 ppm a.e.).

Table 21: AcuteToxicity of Triclopyr to Birds & Honey Bees

Triclopyr Formulation	**Organism**	**LD50**	**Toxicity Ranking**	**Reference/Date Reported**
Acid	Mallard duck	5620 ppm (8-day LC50)	Practically non-toxic	Brian Database, 1979
Acid	Mallard duck	1698 mg/kg (14-day LD50)	Slightly toxic	Brian Database, 1976
Acid	Mallard duck	100 (NOEL) (22 wk study)	Highly toxic	Brian Database, 1979
Acid	Coturnix Quail	3272 ppm (8-day LC50)	Slightly toxic	Brian Database, 1973
Acid	Bobwhite quail	2934 ppm (8-day LC50)	Slightly toxic	Brian Database, 1976
Acid	Bobwhite quail	100 ppm (NOEL) (22 wk study)	Highly toxic	Brian Database, 1979
Acid	Honey Bee	100 ppm (48-hr LD50)	N/A	Brian Database, 1985
Triethylamine salt	Mallard duck	10,000 (8-day LC50)	Practically non-toxic	Brian Database, 1977
Triethylamine salt	Mallard duck	3,176 mg/kg (14-day LD50)	Practically non-toxic	Brian Database, 1978
Triethylamine salt	Mallard duck	1,698 mg/kg (14-day LD50)	Slightly toxic	Brian Database, 1973
Triethylamine salt	Mallard duck	100 ppm(NOEL) (20 weeks)	Highly toxic	Brian Database, 1980
Triethylamine salt	Bobwhite quail	11,622 ppm (8-day LC50)	Practically non-toxic	Brian Database, 1978
Triethylamine salt	Bobwhite quail	500 ppm (NOEL) (19 weeks)	Highly toxic	Brian Database, 1979
Triethylamine salt	Honey bee	100 (48-hr LD50)	N/A	Brian Database, 1985

Table 22: Toxicity of Triclopyr to Plants

Triclopyr Formulation	Organism	LD50	Reference/Date Reported
Triethylamine salt	Sunflower	0.0041 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Onion	0.111 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Wheat	0.0041 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Corn	0.111 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Barley	1.0 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Sugar beet	0.0123 Lb/A NOEL (14 days)	Brian Database, 1993
Triethylamine salt	Soybean	0.00046 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Oilseed rape	0.037 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Radish	0.111 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Sunflower	0.0041 Lb/A (NOEL) (14 days)	Brian Database, 1993
Triethylamine salt	Tomato	0.0041 Lb/A (NOEL) (14 days)	Brian Database, 1993

Table 23: Terrestrial Plant, Bird and Mammal Federally Endangered Species found in the State of Washington

	Common Name	**Scientific Name**
Terrestrial Plants	Ute Ladies'-Tresses	*Spiranthes diluvialis*
	Golden Paintbrush	*Castilleja levisecta*
	Nelson's Checker- Mallow	*Sidalcea nelsoniana*
Birds	Aleutian Canada Goose	*Branta Canadensis Leucopareia*
	American Peregrine Falcon	*Falco peregrinus anatum*
	Bald Eagle	*Haliaeetus leucocephalus*
	Brown Pelican	*Pelecanus occidentalis*
	Marbled Murrelet	*Brachyramphus marmoratus*
	Northern Spotted Owl	*Strix occidentalis caurina*
	Western Snowy Plover	*Charadrius alexandinus nivosus*
Mammals	Gray Wolf	*Canis lupis*
	Grizzly Bear	*Ursus arctos horribilis*
	Woodland Caribou	*Rangifer tarandus caribou*
	Columbian White-Tailed Deer	*Odocoileus virginianus leucurus*

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Appendix 1: Sensitive, Threatened and Endangered Species found in Washington State

Status	**Region**	**Affected Counties within Region**	**Common Name**	**Species**
Endangered	Upper Columbia River	All counties	Spring-run Chinook	*Oncorhynchus tshawytscha*
Endangered	Upper Columbia River	All counties	Steelhead trout	*Oncorhynchus mykiss*
Endangered	Snake River	All counties	Sockeye salmon	*Oncorhynchus nerka*
Threatened				
Threatened	Puget Sound	All Counties	Chinook salmon	*Oncorhynchus tshawytscha*
Threatened	Puget Sound	Clallam, Jefferson, Mason, Kitsap	Hood Canal Summer Chum salmon	*Oncorhynchus kisutch*
Threatened	Puget Sound	All , excluding Kitsap, San Juan, and Island	Bull trout	*Salvelinus confluentus*
Threatened	Washington Coastal	Clallam	Lake Ozette Sockeye salmon	*Oncorhynchus nerka*
Threatened	Washington Coastal	All, excluding Pacific	Bull trout	*Salvelinus confluentus*
Threatened	Lower Columbia River	All counties	Spring-run Chinook salmon	*Oncorhynchus tshawytscha*
Threatened	Lower Columbia River	All counties	Chum salmon	*Oncorhynchus keta*
Threatened	Lower Columbia River	All counties	Steelhead trout	*Oncorhynchus mykiss*
Threatened	Lower Columbia River	All counties	Bull trout	*Salvelinus confluentus*
Threatened	Upper Columbia River	All counties	Bull trout	*Salvelinus confluentus*
Threatened	Middle Columbia River	All counties	Bull trout	*Salvelinus confluentus*

Appendix 1: Sensitive, Threatened and Endangered Species found in Washington State (continued)

Status	Region	Affected Counties within Region	Common Name	Species
Threatened	Middle Columbia River	All counties	Steelhead trout	*Oncorhynchus mykiss*
Threatened	Middle Columbia River	All counties	Bull trout	*Salvelinus confluentus*
Threatened	Snake River	All counties	Spring/Summer-run Chinook salmon	*Oncorhynchus tshawytscha*
Threatened	Snake River	All counties	Fall-run Chinook salmon	*Oncorhynchus tshawytscha*
Threatened	Snake River	All counties	Steelhead trout	*Oncorhynchus mykiss*
Threatened	Snake River	All counties	Bull trout	*Salvelinus confluentus*
Threatened	Northeast Washington	All counties	Bull trout	*Salvelinus confluentus*
Proposed Threatened				
Proposed Threatened	Washington Coastal	Grays Harbor, Pacific, Lewis	Coastal cutthroat trout	*Oncorhynchus clarki*
Proposed as Threatened	Lower Columbia River	All counties	Coastal cutthroat trout	*Oncorhynchus clarki*
Potentially Threatened	Upper Columbia River	Chelan, Okanogan	Westslope cutthroat trout	*Oncorhynchus clarki*
Potentially Threatened	Middle Columbia River	Kittitas, Yakima, Klickitat	Westslope cutthroat trout	*Oncorhynchus clarki*
Potentially Threatened	Northeast Washington	All counties	Westslope cutthroat trout	*Oncorhynchus clarki*
Candidate				
Candidate	Puget Sound	All counties	Coho salmon	*Oncorhynchus kisutch*
Candidate	Washington Coastal	Grays Harbor, Pacific, Lewis, Thurston	Southwest Washington Coho salmon	*Oncorhynchus kisutch*
Candidate	Lower Columbia River	All counties	Coho salmon	*Oncorhynchus kisutch*
Candidate	1[1]	All counties	Pacific Cod	*Gadua macrocephalus*
Candidate	1	All counties	Walleye Pollock	*Theragra chalcogramma*
Candidate	1	All counties	Pacific Hake	*Merluccius productus*
Candidate	1	All counties	Brown Rockfish	*Sebastes* sp.
Candidate	1	All counties	Copper Rockfish	*Sebastes* sp.
Candidate	1	All counties	Quillback Rockfish	*Sebastes* sp.

Appendix 1: Sensitive, Threatened and Endangered Species found in Washington State (continued)

Status	Region	Affected Counties within Region	Common Name	Species
Concern				
Concern	1	All counties	Cherry point herring	Family Clupedidae
Concern	1	All counties	Discovery Bay Herring	Family Clupedidae
Concern	State Wide	All counties	River Lamprey	*Lampetra ayresi*
Concern	State Wide	All counties	Van Dyke's Salamander	*Plethodon vandykei*
Concern	State Wide	All counties	Columbia torrent Salamanader	*Rhyacotriton olympicus*
Concern	State Wide	All counties	Columbia spotted frog	*Rana lutieventris*
Concern	State Wide	All counties	Great Columbia River Spire Snail	N/A[2]
Concern	State Wide	All counties	Newcomb's Littorine Snail	N/A[2]
Concern	State Wide	All counties	California floater	*Adonata californiensis*
Concern	State Wide	All counties	Northern Abalone	*Haliotis sp.*
Concern	State Wide	All counties	Olympia Oyster	*Crassostrea* sp.
State Endangered				
State Endangered	State Wide	All Counties	Oregon spotted frog	*Rana pretiosa*
State Sensitive				
State Sensitive	State Wide	All counties	Pygmy whitefish	*Prosopium coulterii*
State Sensitive	State Wide	All counties	Margined sculpin	*Cottus marginatus*
State Sensitive	State Wide	All counties	Larch Mountain Salamander	*Plethodon larselli*
State Candidate				
State Candidate	State Wide	All counties	Olympic mudminnow	
State Candidate	State Wide	All counties	Mountain sucker	*Catostomus platyrhynchus*
State Candidate	State Wide	All counties	Lake chub	*Coesius plumbeus*
State Candidate	State Wide	All counties	Leopard dace	*Rhinichthys falcatus*
State Candidate	State Wide	All counties	Umatilla dace	*Rhinichthys umatilla*
State Candidate	State Wide	All counties	Eulachon (Columbia River Smelt)	*Thaleichthys pacificus*
State Candidate	1	All counties	Black rockfish	*Sebastes* sp.
State Candidate	1	All counties	Tiger Rockfish	*Sebastes* sp.
State Candidate	1	All counties	Boccacio rockfish	*Sebastes paucispinis*

Appendix 1: Sensitive, Threatened and Endangered Species found in Washington State (continued)

Status	Region	Affected Counties within Region	Common Name	Species
State Candidate	1	All counties	Canary rockfish	*Sebastes* sp.
State Candidate	1	All counties	Yellowtail rockfish	*Sebastes* sp.
State Candidate	1	All counties	Greenstriped rockfish	*Sebastes* sp.
State Candidate	1	All counties	Widow rockfish	*Sebastes* sp.
State Candidate	1	All counties	China rockfish	*Sebastes* sp.
State Candidate	State Wide	All counties	Dunn's Salamander	*Plethodon dunni*
State Candidate	State Wide	All counties	Cascade torrent salamander	*Rhyacotriton cascadae*
State Candidate Under Review	State Wide	All counties	Northern Leopard Frog	*Rana pipiens*
State Candidate	State Wide	All counties	Giant Columbia River Limpet	N/A[2]

[1] Within Puget Sound, the San Juan Islands, and the Strait of Juan de Fuca east of the Seiku River
[2] N/A = Not available

Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides

TRICLOPYR

Volume 5, Section 5

HUMAN HEALTH EFFECTS

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5.0 HUMAN HEALTH EFFECTS

5.1 OBJECTIVE

The Washington State Department of Ecology (WDOE) contracted with Compliance Services International (CSI) to prepare a document concerning potential human health impacts from aquatic application of the herbicide triclopyr. Renovate®Aquatic Herbicide is the triclopyr herbicide formulation used for control in the State of Washington. The product contains 44.4%, by weight, triclopyr triethylamine salt (TEA). This concentration of TEA is equivalent to 31.8%, by weight, of triclopyr acid or the acid equivalent (ae). TEA rapidly undergoes hydrolysis following application in the aquatic environment to the triclopyr acid or acid equivalent (Solomon, 1988; Woodburn, 1993a,b; Petty, 1998).

Triclopyr acid may undergo further degradation to 3,5,6-trichloro-2-pyridinol (TCP) and 3,4,5-trichloro-2-methoxypridine (TMP). TCP and TMP are rapidly degraded by photolysis and/or biotransformation and are considered to have less toxicity than the triclopyr parent molecule (EPA, 1998).

Since triclopyr (ae) is the active ingredient in the formulation, discussions concerning the subchronic and chronic toxicology, exposure assessments and risk assessments will be in terms of triclopyr (ae) or simply triclopyr. Discussion concerning TEA refers to the applied product and the results of the acute toxicology testing where findings are used to classify and label the product according to the EPA Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) guidelines. In summary, when the word “triclopyr” appears in this document, it refers to the triclopyr acid.

The human health section is designed to provide the most recent health information to the WDOE concerning the toxicology of triclopyr and potential health risks to the public associated with triclopyr aquatic weed control. It is also the intent of this section to assist the agencies in making decisions regarding continued triclopyr uses and establishing various swimming alerts and waiting periods for water use following herbicide application to bodies of water.

The objectives of this section are to: 1) provide a review of the available triclopyr toxicology information, 2) determine the degree and types of potential exposures that may be encountered during various time periods following TEA aquatic application, and 3) present a series of risk assessments of the different types of exposures to aquatic applied triclopyr and determine any need or recommendations for mitigation of exposure to ensure public health.

5.2 APPROACH

5.2.1 Information Compilation

Information concerning triclopyr toxicology and health effects were obtained from computerized searches of the scientific and medical literature, EPA Office of Pesticide Programs, Washington State Department of Health (WDOH),WDOE and the herbicide registrant Dow Agrosciences.

5.2.2 Risk Assessment Procedure

5.2.2.1 Triclopyr Toxicology Information and Assessment

Section 1 of this document discusses the registration and regulation of pesticides. Part of registering any pesticide with the US Environmental Protection Agency (US EPA) involves the potential registrant conducting a series of required toxicology studies. One of EPA's functions is to ensure that all pesticides be registered in accordance with FIFRA guidelines. The series of toxicology studies include acute (one exposure), subchronic (multiple exposures, e.g. weeks or months) and chronic exposure to the chemical over the entire lifetime of the animal. The subchronic and chronic studies were conducted on technical triclopyr or the triclopyr acid or acid equivalent.

In addition, once the technical chemical or active ingredient has been registered for specific uses with the EPA, various product formulations of the active ingredient can be prepared, tested for efficacy and acute toxicology. The results of the acute toxicology studies, see Table 1 (oral, dermal, inhalation, skin and eye irritation and skin sensitization studies), are used to evaluate the health hazards that may be associated with overexposure to the applicator, bystanders and others that may contact treated areas following application of the pesticide. Once the hazards have been determined by the results of the tests, the specific product label warnings are then determined by FIFRA guidelines and serve to alert the consumer as to the associated product health hazards and precautions to take to prevent overexposure.

The triclopyr product label "Renovate® Aquatic Herbicide" bears the "DANGER" signal word and precautionary statements alerting the user that, depending upon the degree and duration of overexposure to the concentrated product, the chemical is "Corrosive. Causes irreversible eye damage. Prolonged or frequently repeated skin contact with the herbicide concentrate may cause an allergic skin reaction in some individuals."

Medical and toxicology literature report a number of incidents involving human oral and dermal overexposure to triclopyr. The human clinical toxicology of triclopyr is discussed in Section 5.17. Since there are no triclopyr epidemiology investigations or worker exposure studies, the potential human exposure to triclopyr treated water has been derived from the chemical use-rates and findings from the triclopyr aquatic analytical studies. Risk assessments were calculated based on various types and routes of triclopyr aquatic exposure and findings from animal laboratory toxicology studies.

As described in Section 1 of this document, animal toxicology studies are typically designed to include low, mid and high dose test groups. The objective of having at least 3 dose groups is to determine the health effects observed and measured by the various degrees of exposure. The high dose group receives an amount of test material designed to overwhelm the body defense mechanisms, e.g. in suicide attempts, while the low dose is intended to not cause any observable or quantitated adverse health effects. The low dose or dose level that does not demonstrate toxicological effects is termed the no observable adverse effect (NOAEL or NOEL). The NOAEL is used in risk assessment calculations and sometimes is adjusted with an uncertainty factor(s) (UF) to compensate for extrapolation of calculated "safe" dose levels to humans from various animals species and toxicology endpoints, e.g. systemic toxicity, reproductive and fetal developmental effects, cancer, etc.

The triclopyr toxicology investigations are discussed in the following sections and the NOAELs and toxicology endpoints listed in Tables 2 and 4.

5.2.2.2 Exposure Assessment

The exposure assessment involves determination of populations that may be exposed to triclopyr, estimating degrees of exposure and doses likely to result from the various uses of the herbicide products following aquatic weed control. The exposure parameters evaluated in this section are listed in Tables 3 and 5 and include governmental health advisories and exposure parameters.

Exposure assessments for herbicidal use assume the maximum triclopyr triethylamine salt (TEA) use-rate of 2 gallons TEA/acre or 6 pound triclopyr acid equivalent/acre of surface water treated for aquatic weed control. The immediate maximum triclopyr concentration at the highest use-rate is approximately 2.5 ppm (Renovate® label, 1997). Based on the assumed use-rates, exposure calculations were conducted for swimmers and bystanders or non-swimmers regarding their daily exposure to triclopyr. Swimmers were expected to spend anywhere from 0.5 to 3 hours swimming in triclopyr treated water. Routes of exposure include dermal contact and incidental ingestion of treated water, dietary drinking of potable or treated surface water and ingestion of fish taken from treated water. All subjects are divided into three groups consisting of 6 (22 kilogram weight) and 10 (35 kg) year olds and adults (70 kg).

The maximum exposure conditions included swimmers either daily drinking potable or treated surface water containing the maximum aquatic herbicidal use-rate of 2.5 mg/L (2.5 ppb; 2500 ug/L; 2.5 ug/ml) or the Allowable Residue Level in Drinking Water (ARLDW) of 0.5 ppm or 0.5 mg/L or 500 ug/L. Also, the exposure from eating fish taken from triclopyr treated water was calculated (see Table 11). Since triclopyr is not intended to be used on food crops and does not bioconcentrate in living organisms, other potential dietary sources of exposure were not conducted.

Tables 12 and 13 present the combined sources of triclopyr exposure. The main factor in the exposure to triclopyr following aquatic application for weed control concerns the incidental ingestion of water by the swimmer and ingestion of daily drinking water from either potable (containing 500 ug triclopyr/L) or triclopyr treated surface water (containing 2500 ug triclopyr/L).

5.2.2.3 Risk Characterization

The potential risk of non-carcinogenic effects is usually evaluated by comparing an environmental dose to a reference or “safe” dose. In the risk assessments for various triclopyr aquatic exposure doses the margin of safety (MOS) and reference dose (RfD) approaches were used.

The MOS is used to evaluate acute exposures. In this approach the lowest NOAEL or NOEL from the animal toxicology studies for specific endpoints, e.g. systemic toxicity, reproduction or developmental, were compared to the calculated human triclopyr doses. This method allows an evaluation and determination of a “safe” dose specific to each human route of exposure. Thus, the MOS is a ratio of the lowest NOAEL dose to the calculated exposure dose and is meant to be an indicator of potential risk. The standard MOS is 100, meaning that MOSs greater than 100 represent degrees of negligible risk, while values below 100 signal an increased risk of the toxic endpoint effects (Shipp, 1986). MOS findings are included in calculations in Tables 6-13.

The reference dose or RfD represents a lifetime "safe" dose for protection against threshold (non-carcinogenic) health effects. The RfD is considered a daily exposure level for a lifetime where no adverse health effects are likely to occur for even sensitive human populations. Under the RfD approach a UF may be applied to the lowest NOAEL dose reported in the animal toxicology studies. A UF of 10 is generally used to estimate a "safe" human exposure level from experimental studies when there is no indication of carcinogenicity and valid human studies are available. A more conservative UF of 100 is supplied when there are few or no valid human studies available but there are valid long-term animal studies. In the case of triclopyr, since no human exposure studies have been conducted, the 100 UF was applied.

In the calculations in Tables 6-13 the percentage of the daily RfD is presented for the various types of exposure doses. Percentages below 100% of the RfD are considered negligible health risks while those greater than 100% serve as indicators that a potential health risk may exist at the specific exposure dose. Tables 12 and 13 include combined types of exposures and total daily triclopyr doses with their accompanying MOS and RfD risk assessments.

5.3 CHEMICAL FORMULATIONS

The only triclopyr product currently used for aquatic weed control in the State of Washington is Renovate® Aquatic Herbicide. The formulation contains 3 lbs/gallon of triclopyr acid equivalent. Dose levels and water concentrations are defined in terms of triclopyr acid equivalent. Triclopyr concentrations discussed and presented in this document are in terms of triclopyr acid equivalents. The triclopyr maximum use-rate for aquatic herbicide control is 6 pounds acid equivalent/acre. Using the highest Renovate® use-rate, the instantaneous maximum water concentration is considered to be 2.5 mg/liter or 2.5 parts per million (ppm) of treated water, and depending upon the water environmental conditions, decrease to approximately 0.4 ppm after 24 hours to 4 days. However, the ARLDW of 500 ug/L has been used to calculate exposure to treated water beyond the first day following treatment.

5.4 EXPOSURE ASSESSMENT

Exposure assessments were conducted on three populations that included children and adults. The children were ages 6 and 10 weighing 22 and 35 kg, respectively and 70 kg for adults. The population groups were evaluated according to their time spent swimming in triclopyr treated water containing 2.5 ppm and in cases beyond 24-hours following application of 0.5 ppm. Routes and types of exposure included incidental ingestion and skin contact with treated water. In addition, the population groups were also evaluated as to their exposure received from drinking potable water or treated surface water and daily consumption of fish taken from treated water. Exposure assessments appear in Tables 6-13.

5.5 EXPOSED POPULATION

The exposed population in this section refers to the general public and does not include people who may be occupationally exposed during mixing, loading or applying triclopyr to bodies of water. The exposed populations used in the exposure assessment are described in Section 5.4.

5.6 POTENTIAL ROUTES OF EXPOSURE

The primary potential route of exposure to the exposed population groups was ingestion of triclopyr treated water either during swimming or through daily use of potable or treated water as a drinking water sources. Other potential routes of exposure included dermal contact of treated water and eating fish taken from the treated water.

The calculated doses received by the exposed population groups are discussed in Section 5.18 and presented in Tables 6-13.

5.7 TOXICITY ASSESSMENT

The animal toxicology information concerning triclopyr is discussed in the following subsections and consists of a review of acute, subchronic and chronic testing. An overview of the toxicology information indicates that the chemical is not considered to be a carcinogen, mutagen or to cause adverse reproductive effects or birth defects (teratology). Triclopyr is considered to have a low degree of systemic toxicity based on findings from the acute and subchronic toxicology studies (Tables 2 and 4).The main adverse health effect appears to be associated with eye contact with the concentrated Renovate® formulation which can result in severe eye irritation and damage. Results of the undiluted triclopyr product acute eye irritation studies place the chemical in FIFRA Toxicity Category I as causing irreversible eye damage.

There are four FIFRA Toxicity Categories numbered I-IV. Category I designates pesticides being the most toxic or irritating, while Category IV represents the least toxicity or irritating chemicals. Pesticides in Categories II and III fall in between the two extremes. See Table I for triclopyr acute toxicology findings and FIFRA toxicity category classifications. Contrary to the results of the acute rabbit eye irritation study, the findings from the rabbit skin irritation test reveal minimal irritation placing the skin irritation potential in Category IV. The FIFRA acute oral and dermal systemic toxicity of the concentrated triclopyr are Toxicity Categories III and IV, respectively. A further reduction in the systemic toxicity and eye irritation potential of triclopyr occurs when Renovate® is used according to the label directions for aquatic weed control where dilution and degradation of the chemical takes place in the water and sediment following application, thus significantly reducing the potential for overexposure.

5.8 PHARMACOKINETICS

5.8.1 Absorption, Distribution and Metabolism

- **Oral**

Results of pharmacokinetic triclopyr oral dosing investigations demonstrate that the chemical is rapidly absorbed from the gut and primarily excreted in the urine as the parent compound. Smith et al, (1992) using 14C-triclopyr, administered a dose of 3 mg/kg to rats and found that plasma triclopyr levels peaked within 0.5 hours and 91%-94% of the dose was excreted in the urine with an average half-life of 10 hours. The remainder of the labeled triclopyr was found in the feces (2%), skin (1.2%) and cage wash (0.7%).

Timchalk et al (1997a) determined that the dog and monkey are affected differently with regard to renal excretion of triclopyr. The investigation involved subchronic oral administration of triclopyr to dogs at a level of 5 mg/kg/dy for 28 days and then the dose was increased to 20 mg/kg/dy for 47 days. Monkeys received a triclopyr dose of 5 mg/kg/dy orally for 28 days followed by an increased amount of 20 mg/kg/dy for 102 days. Results of the study indicated that repeated administration of triclopyr had no effect on the glomerular filtration rate in either species. Also, it was determined that triclopyr did not compete with exogenous phenolsulfonphthalein (PSP) or para-aminohippurate (PAH) for the active secretory site in the kidney proximal tubules. However, this was not the case in the dog where triclopyr and PSP competed for the active secretory site, thus indicating that the dog differs in this particular renal function activity in comparison to the monkey. The competitive secretory activity was not considered a toxic effect.

Timchalk and Nolan (1997b) further demonstrated that the pharmacokinetics of triclopyr in the dog are different than in the rat, monkey and humans. 14C-triclopyr was administered in a single oral dose to dogs at levels of 0, 0.5, 5 and 20 mg/kg and 30 mg/kg i.v. to a monkey. Results of the study demonstrated that >95% and nearly all of the triclopyr was excreted in the urine by 24 and 72 hours in the monkey and dog, respectively. In the dog 94%-99% of the triclopyr was bound to the plasma protein and became an important factor in renal excretion of the chemical. As plasma triclopyr concentrations increased, tubular reabsorption began to exceed secretion resulting in decreased renal clearance of the chemical. The rate of triclopyr renal clearance and plasma half-life in the rat, monkey and human could be calculated based on volume distribution normalized to body weight. However, due to the findings of slower triclopyr clearance and plasma half-life, the same modeling calculations did not predict the rates for the dog.

Timchalk et al (1988) also conducted a similar investigation using 14C-triclopyr in rats where dose groups included 3 and 60 mg/kg. They found that the chemical was quickly absorbed, did not undergo significant metabolism and 89%-95% excreted in the urine by 72 hours. The urinary half-life for the study was 3.6 hours.

Timchalk et al (1988) and Landry et al (1984) conducted subchronic pharmacokinetic investigations administering rats oral dose levels of 14C-triclopyr of 3 mg/kg/dy/14 dys and 50 and 250 mg/kg/dy/28 dys. The results of the investigations were similar to the triclopyr acute pharmacokinetic studies. The only difference appeared to be that at high dose levels the chemical tends to saturate renal capacity to excrete the chemical, demonstrating slight non-linear elimination rates. There was no evidence between acute and subchronic dosing as to rate of absorption, distribution, metabolism, deposition or excretion.

Carmichael et al (1988) conducted a human oral dosing study administering 0.1 and 0.5 mg/kg triclopyr. The investigators determined that blood levels of the chemical peaked 2-3 hours following dosing. Triclopyr was excreted unchanged in the urine where 80% and 83.5% of the low and high dose were eliminated by 72 hours, respectively. The urinary triclopyr half-life in the human investigation was 5 hours. None of the subjects experienced any adverse health effects. Results of hematology, biochemistry and urinalysis before, during and two weeks after the study were normal.

van Beck et al (1981) dosed rabbits intravenously with 30 mg/kg of triclopyr and found that greater than 90% of the dose was excreted unchanged in the urine by 8 hours following dosing. Triclopyr urinary excretion was essentially complete by 24 hours.

5.8.2 Dermal

Triclopyr is poorly absorbed through skin. Results of rabbit acute and subchronic investigations and a human dermal penetration study revealed that the chemical does not readily absorb through skin. van Beck and Leegwater (1981a) demonstrated that a single dermal application of 2,000 mg/kg of triclopyr to the skin of rabbits for 24 hours resulted in < 2% of the dose recovered in the urine at the end of the test period. Similarly, when van Beck et al (1981b) conducted a triclopyr subchronic rabbit dermal study applying doses of 125, 250 or 500 mg/kg/dy/5 dys/wk/ 3 wks and collected 24-hour urine samples, they found that an average of 8.5% of the daily dose was recovered in the urine in all dose groups.

Carmichael et al (1988) conducted a human volunteer triclopyr dermal absorption study where 5 mg/kg (0.8 ml) of the chemical was applied to the forearm for 8 hours. The results indicated that the chemical was first determined analytically in the blood by 2 hours, peaked at 12 hours and undetected at 72 hours. The urinary analyses revealed that peak triclopyr concentrations were attained between 12 and 24 hours and decreased to barely detectable amounts by 96 hours. An average of 1.37% of the applied triclopyr dose was recovered in the urine by 96 hours.

In summary, it appears that the pharmacokinetic dynamics of triclopyr are essentially consistent in all species tested. Renal excretion is the primary route of removal of triclopyr from the system. Results from pharmacokinetic investigations indicated that approximately 80%-90% of the recovered dose is voided in the urine predominantly as the parent compound. Fecal excretion increases progressively as the dose of triclopyr increases to saturate the renal excretory capacity. However, at non-renal saturating doses the chemical is nearly completely excreted by 24 hours. Although triclopyr acid is primarily excreted unchanged, there are minor metabolites of the pyridinol metabolites and/or conjugated derivatives also present.

5.9 SYNERGISM WITH OTHER PESTICIDES

A review of the scientific and medical literature indicates that there have been no investigations conducted to determine the potential of either triclopyr or its products to interact synergistically with other chemicals.

5.10 ACUTE TOXICITY

Results of the triclopyr acute toxicology studies demonstrate that the chemical is considered to be slightly toxic and has significant eye irritation potential (see Table 1). The findings from the rat acute oral and dermal toxicity studies classed the chemical in FIFRA Toxicity Categories III and IV, respectively. Findings from the triclopyr rabbit skin irritation and rat acute 4-hour aerosol inhalation investigations class the chemical in FIFRA Toxicity Category IV. However, the results of the rabbit eye irritation study demonstrate that the formulation is a Category I eye irritant.

The rabbit eye irritation investigation is designed to mimic extensive exposure to the concentrated chemical. The test consists of putting a small amount of chemical in one eye of the animal, leaving it there, not rinsing the eye, and then note any gross ocular changes over a 21-day observation period. Table 1 lists the triclopyr acute toxicology studies findings and the designated FIFRA Toxicity Categories. Based on the findings from the acute toxicology studies and the FIFRA categorization, the triclopyr product label DANGER signal word and precautionary statements are determined.

As stated in Section 1 of the WDOE Aquatic Herbicide EIS, one of the objectives of conducting acute toxicology studies is to determine the “LD50” of a chemical. The LD50 is defined as the “lethal dose” that kills or calculated to kill half or 50% of the animal test population. The LD50 is a universal guide in toxicology that commonly serves to categorize the degree of acute toxicity of a particular chemical or product. LD50s are determined for both the oral and dermal routes of exposure. LC50s or lethal concentrations of airborne chemical vapor, aerosol or dust define the acute amount or dose of respirable chemical that kills half or 50% of the animal test population. The LD50 and LC50 doses determine placement of a pesticide in FIFRA Toxicity Categories I –IV.

It is important to understand that the results of the acute toxicology studies reflect the health effects following overexposure to the concentrate or undiluted chemical or product. In most cases, the acute toxicology studies represent the worst case exposure conditions.

In contrast to results of acute toxicology testing, immediate contact with triclopyr treated water would be significantly reduced in degree of toxicity and irritation potential because of the water dilution factor. In addition, the amount of triclopyr in the treated water would decrease due to the chemical’s half-life that ranges from <1.3 to 4.7 days. The reduction of triclopyr in water is due to the massive dilution factor of the water, rapid hydrolysis and photolysis to triclopyr acid and oxamic acid and carboxylic acids (Woodburn, 1993a; Woodburn, 1993b; Solomon, 1988; Petty, 1998). Due to the rapid breakdown of aquatically applied triclopyr, the chance of overexposure to the chemical from contacting treated water significantly reduces the availability of the chemical and chance for eye overexposure.

Human overexposure to concentrated or undiluted triclopyr during application can result from accidental spilling or splashing of the chemical on the skin, in the eyes or in the mouth. Regardless of the route of overexposure, the first aid procedures outlined on the triclopyr product label should be followed immediately and where indicated, the exposed person should be examined by a physician.

Also, depending upon the spray equipment settings and wind factors, the applicator may be overexposed to the triclopyr spray mist during application of the product over the surface of the water. The degree and duration of overexposure to the concentrated triclopyr spray mist determines the extent of any signs and symptoms of irritation to the eyes and upper respiratory tract and possible systemic toxicity. However, spray application of triclopyr by boat, involves equipment that forms large spray droplets that can be easily directed to the targeted aquatic treatment area. It is counter productive to apply smaller size spray droplets that would minimize the amount of herbicide contacting the designated treatment area and may result in formation of spray drift and the potential for triclopyr overexposure to the applicator or area bystanders and non-target vegetation.

5.10.1 Oral Toxicity

The findings from the triclopyr acute oral toxicology investigations indicate that ingestion of large amounts of concentrated formulation may be irritating to the stomach and intestinal tract, and depending upon the dose, can result systemic poisoning and death. Mizell (1988) conducted a rat acute oral toxicity study using Garlon® 3A (contains 44.4% triclopyr triethylamine salt; equivalent to 32.3% a.e.) and determined the LD50 to be 2,574 and 1,847 mg/kg in the male and female animals, respectively. Rats that died during the study revealed gastric irritation at gross autopsy. Surviving animals had no treatment-related pathologic changes. Signs include stress, decrease in body weight, reduction in water and food intake. Surviving animals were normal at the end of the 14-day observation period.

Based on the findings in the triclopyr rat acute oral toxicity study, the Garlon 3A and Renovate formulations are classed in EPA FIFRA Toxicity Category III.

Although there are no reports in the medical and scientific literature regarding human ingestion of triclopyr, accidental or suicidal ingestion of large amounts of concentrated chemical may result in irritation of the digestive tract that clinically may be manifested by nausea, vomiting, abdominal discomfort and diarrhea. Since the chemical is rapidly absorbed from the stomach, large doses may overwhelm the renal mechanism of excretion and have adverse affects on the liver and kidneys.

5.10.2 Dermal Toxicity

Systemic toxicity from dermal exposure to triclopyr was not demonstrated in any of the laboratory acute and subchronic toxicology studies (Mizell, 1989(a); Gilbert, 1996; Lockwood, 1992). The acute dermal LD50 was > 5,000 mg/kg (Gilbert, 1996). Due to the concentration of the dose that remained in contact with the skin for 24 hours, observation of erythema, edema, burns, scabs and scales were noted. Based on the triclopyr acute dermal LD50 of >5,000 mg/kg, the product is classed in FIFRA Toxicity Category IV. The subchronic dermal investigation involved application of triclopyr at a dose of 1,000 mg/kg/6 hr/dy/4 dys to the skin of rabbits. Although no signs of systemic toxicity were observed, Lockwood reported dermal irritation consisting of moderate to severe erythema and moderate necrosis occurred at the site of application. Due to the severe skin irritation, the study was terminated at day 4 instead of the prescribed 21 days.

The absence of systemic toxicity in the dermal toxicity studies, support the pharmacokinetic findings that triclopyr has a low rate of dermal penetration.

5.10.3 Inhalation Toxicity

Inhalation overexposure to triclopyr spray mist during labeled directed use for aquatic herbicide weed control is not expected to be a significant health risk. The size of spray droplets for aquatic application must be sufficiently large so that they fall directly on the intended target area. This is also to prevent human exposure and drift to non-target areas. Aquatic use of triclopyr for weed control is primarily done by subsurface application or underwater injection.

Since triclopyr has a very low vapor pressure of 1.26 x 10-6 mmHg @ 25^oC, the chemical vapor is not expected to be a health problem (Chakrabarti, 1988).

The rat acute inhalation toxicity study involved a 4-hour exposure to respirable triclopyr aerosol particles (Nitschke, 1989). The animals displayed signs of ocular and nasal discharge during the first day and some decrease in body weights on day 2 of the observation period. At the end of the 14-day observation period no gross pathological changes were noted. The 4-hour LC50 was >2.6 mg/l, placing the formulation in FIFRA Inhalation Toxicity Category IV.

Based on the results of the triclopyr rat acute inhalation study, the type of aquatic weed control spray application and the large size of the spray droplets, it is unlikely that applicator workers or bystanders will be overexposed to triclopyr during aquatic herbicidal spraying.

The aerosol particle sizes generated in the animal inhalation study were nearly all respirable (less than or equal to 10 microns in diameter), while typical agricultural spray equipment delivers particles in the size range of 200 microns. In the case of triclopyr spray application to bodies of water, the particle sizes would be much greater than 200 microns for reasons described above, thus minimizing formation of respirable particles. Due to the design of the mammalian respiratory tract, particles less than 10 microns are required to reach the air sacs or alveoli of the lung. Larger particles of 200 microns and greater are deposited in the nasal passages and throat of the upper respiratory tract.

As with the oral and dermal routes of exposure, there are no substantiated reports of human triclopyr systemic poisoning following acute or repeated inhalation exposure to the chemical spray mist or particles.

5.10.4 Skin Irritation

A review of the rabbit toxicology dermal irritation study concerning triclopyr indicate that the formulation was not irritating to the skin of rabbits following contact with the concentrate for 4 hours (Mizell, 1988). The results of the investigation class triclopyr in FIFRA Toxicity Category IV for skin irritation.

5.10.5 Eye Irritation

Based on the results of rabbit eye irritation study, concentrated triclopyr is considered to be a severe eye irritant and classed in EPA FIFRA Toxicity Category I. Because of the severe eye irritation potential of the concentrated product the Renovate® label bears the "DANGER" signal word and precautionary warning statements: "Corrosive. Causes Irreversible Eye Damage." The findings from the triclopyr eye irritation study demonstrated slight to marked conjunctivitis, edema of the ocular tissues, reddening of the iris and discharge. Slight to severe corneal opacity was present in all animals. At day 7 the animals with severe corneal involvement were sacrificed. At the end of the 21-day observation period all eyes were normal except for one animal that had scattered areas of corneal opacity (Mizell, 1988).

Henck (1980a, 1980b), conducted rabbit eye irritation studies using 1:3 and 1:7 dilutions of triclopyr. Results of the investigations revealed that animal eyes treated with the 1:3 triclopyr dilutions initially demonstrated moderate conjunctival redness and swelling and corneal injury. All eyes were normal by day 7 post-application including the absence of corneal involvement. Results of the investigation using 1:7 dilution of triclopyr revealed initial very slight conjunctival redness and corneal injury. At the 24-hour observation period all eyes were normal.

Significant ocular irritation is not expected from eye contact with triclopyr treated water because of the rapid dissipation and breakdown of the chemical by means of dilution, hydrolysis, photolysis and absorption into the aquatic vegetation.

5.10.6 Skin Sensitization

Results of the triclopyr guinea pig skin sensitization studies indicate that the chemical has skin sensitization potential (Mizell, 1989; Berdasco, 1994). Berdasco (1990a; 1990b) provided evidence that dilution of the chemical also reduced the potential for triclopyr to cause skin sensitization. Berdasco (1990a,b) demonstrated that guinea pigs treated with triclopyr dilutions of 15% and 30%, did not display evidence of skin sensitization.

Therefore, based on the results of the guinea pig skin sensitization investigations, the low product use rates, water dilution factor, hydrolysis and photolysis and incorporation of chemical into vegetation, allergic skin reactions are not expected from persons contacting triclopyr treated water. Nevertheless, the findings of Mizell (1989b) and Berdasco (1994) were sufficient to require that the Renovate® product label have the precautionary warning statement; "May cause an allergic skin reaction in some individuals."

5.11 SUBCHRONIC TOXICITY

Subchronic or repeated daily or weekly chemical exposures for short time periods typically occur during the application of a chemical or through dietary intake of a treated food crop or water. Most human chemical exposures are either acute (one time exposure) or subchronic (exposure to a chemical for a few days or weeks). The potential for subchronic exposure to triclopyr when used for aquatic weed control is unlikely since the chemical dissipates quickly having a half-life of approximately 0.5-5 days in natural waters. Aquatically applied triclopyr is essentially undetectable by 14 days (Petty, 1998).

Significant exposure to persons in contact with recently triclopyr treated water would primarily involve dermal contact and incidental ingestion of the chemical while swimming, drinking contaminated potable or treated water as a daily drinking water source or ingestion of fish taken from treated water.

Inhalation exposures to triclopyr in aquatic herbicidal use situations basically applies to field applicators where possible generation of a spray mist may occur. However, aquatic application of triclopyr in compliance with label directions is not expected to result in adverse health effects following contact with treated water. Further factors mitigating against any adverse health effects from applied triclopyr are the significant water dilution, poor dermal and gut absorption, rapid excretion of absorbed triclopyr and short half-life in water all support the conclusion that overexposure to the chemical is unlikely.

Subchronic toxicology studies are designed to determine the target organ(s) associated with overexposure to a chemical for a few weeks or months. Such studies usually consist of four groups of animals, a control (non-exposed group) and low, mid and high dose test groups. The parameters of subchronic investigations are designed to define the dose and associated toxic effects of the chemical, identify the specific target organ(s) affected, note signs of toxicity, changes in body weight and food consumption, blood chemistry and urine analyses, hematology and gross and histopathological examination.

Based on the results, the target organ(s) associated with overexposure to the test compound can be identified and a no observable adverse effect level (NOAEL) dose can be determined for the chemical. The findings from the investigation can also be used for determining the degree of toxicity of the chemical, risk assessments, establishment of acceptable exposure levels, dietary and drinking water standards, label precautionary statements and other sources of health information.

5.11.1 Oral

Results of a rat triclopyr 13-week dietary feeding study consisting of dose groups of 0, 5, 20, 50, 200 or 300 mg/kg/dy demonstrated that animals in the 2 high dose groups displayed signs of decreased food consumption and body weight gain (Landry, 1984a). None of the animals demonstrated any signs of systemic toxicity. Findings from the three high dose group males revealed increased relative kidney weights and degeneration of the proximal tubules. The degenerative tubule changes were also observed in the female rats receiving doses of 20 mg/kg/dy and greater. The investigators speculated that the renal hypertrophy may have been a compensatory change in response to maintaining excretion of elevated levels of triclopyr and normal physiological function.

The high dose male rats also demonstrated histological alterations of the centrilobular hepatocytes. The liver changes were also accompanied by increased SGTP levels. The liver effects further revealed a possible direct systemic toxic affect as an adaptive response to accommodate the biotransformation and clearance of an increasing body burden of triclopyr. Based on the results of the investigation, the systemic NOEL and LOEL were 5.0 and 20 mg/kg/dy, respectively, as evidenced by the histopathological changes in the kidneys (Landry, 1984a).

Quast et al (1976), conducted a 228-day (7.6 months) dog triclopyr dietary feeding study where dose levels of 0, 5, 10 or 20 mg/kg/dy were administered. Findings from the investigation indicated that there were minimal treatment-related changes at all dose levels. The changes included decreases in food consumption and body weights, liver and kidney weight variations, some blood chemistry changes and histopathological observations in the kidneys and liver. Renal histopathology observations included cloudy swelling of the epithelial cells of the proximal and distal convoluted tubules, while liver changes revealed coagulation necrosis and proliferation of the reticuloendothelial cells lining the sinusoids. Based on the clinical and histopathological findings a NOAEL could not be determined.

Since a NOAEL was not established in the 228-day dog triclopyr feeding study, Quast (1977) conducted a 183-day (6 month) dog investigation using the same protocol and administering dietary doses of 0, 0.1, 0.5 or 2.5 mg/kg/dy. The results of the second dog investigation demonstrated no significant treatment-related effects except for a decrease in phenolsulfonthalein (PSP) excretion in the high dose group dogs. This finding was judged to be renal competition between triclopyr and PSP excretion and not a toxicological effect. The triclopyr systemic NOAEL and LOEL for the study was 2.5 mg/kg/dy.

Quast (1988) next conducted a triclopyr 1-year dog dietary feeding study where dose levels of the chemical included 0, 0.5, 2.5 or 5.0 mg/kg/dy. There were no significant adverse health effects associated with administration of the chemical based on clinical signs, food intake, body weights, blood chemistry or histopathology. Changes reported in clinical chemistry parameters of BUN, creatinine and PSP excretion were judged to represent physiological responses to the limited ability of the kidneys to excrete the body burden of triclopyr and maintain normal physiological function. There were no histopathological liver or kidney findings considered toxicologically significant. The systemic NOAEL and LOEL for the study was 5.0 mg/kg/dy (EPA, 1998).

5.11.2 Dermal

van Beck et al (1984) conducted a 21-day rat subchronic triclopyr dermal study with dose levels of 0, 17, 171or 342 mg triclopyr acid equivalent/kg/dy. The test material was allowed to remain in contact with the skin for 7 hours prior to the treated dermal site being rinsed with water. There were no signs of toxicity or deaths during the 21-day test period. However, a dose-response degree of dermal irritation was observed by the presence of erythema, edema, scaliness and/or incrustation. Histologically, the dermal effects were consistent with a chronic inflammatory reaction with or without accompanying acanthosis, epidermal necrosis and crusting. There was a noted dose related decrease in body weight gain in all treated males and mid and high dose females. The changes were considered a response to discomfort from the degree of skin irritation and not due to systemic toxicity. There was also some increase in SGOT and SGPT liver enzymes in treated animals. These investigators indicated that the elevation in liver enzymes might have been a response to the impaired nutritional status of some of the treated animals.

Gross pathology revealed increased kidney weights in high dose treated animals. The renal weight changes were thought to be compensatory hypertrophy to accommodate the clearance of triclopyr and maintenance of physiological function. Histopathological examination of the kidneys and liver did not reveal any treatment-related changes. The investigators did not propose any NOAEL or LOEL since changes in body weight, liver enzymes and kidney weights were not conclusively associated with either systemic toxicity or discomfort from the dermal irritation.

5.11.3 Inhalation

No subchronic triclopyr inhalation toxicology studies have been conducted because subchronic exposure is unlikely due to the way the chemical is used and applied. Triclopyr is primarily injected as a means of tree and brush control, thus minimizing any mist or vapor exposure. Other reasons for the absence of triclopyr subchronic inhalation investigations are the low vapor pressure (1.26 x 10-6 mmHg @ 25^{o}C), low volatility from treated areas and use of large spray droplets for aquatic weed control (WDOH, 1999).

5.11.4 Neurotoxicity

Results of the triclopyr acute, subchronic and chronic toxicology investigations revealed that overexposure resulted in kidney and liver effects. No findings of neurological changes were reported either from observation of the treated animals during the post-dosing study periods or findings from histopathology. Therefore, due to the lack of neurological effects, no triclopyr neurotoxicity studies have been conducted.

5.11.5 Immunotoxicity

A review of the animal toxicology studies and scientific and medical literature does not indicate that any specific triclopyr immunotoxicity investigations have been conducted. However, based on the negative findings from the subchronic, chronic, multigenerational reproduction and mutagenicity toxicology investigation, it seems unlikely that triclopyr has significant immunotoxic potential.

5.11.6 Estrogen Disruption

There is no evidence or results from toxicology testing that demonstrates overexposure to triclopyr results in any findings or changes associated with adverse endocrine function or mimicking effects. The results of the triclopyr teratology and reproduction studies did not provide any evidence that the chemical demonstrated teratogenic potential or reproductive changes. Similarly, results of the subchronic and chronic investigations did not reveal any findings of behavioral, clinical or histopathological changes considered to be associated with adverse endocrine effects.

5.12 CHRONIC TOXICITY

The chronic or lifetime exposure effects from triclopyr have been evaluated in the mouse and rat. The findings from the investigations are consistent in that long-term exposure to triclopyr did not demonstrate any evidence that triclopyr has carcinogenic potential (Goodman, 1996).

A 2-year rat triclopyr dietary feeding study (Eisenbrandt, 1987), demonstrated that when animals were dosed at treatment groups of 0, 3, 12 or 36 mg/kg/dy, mid and high dose males had increased absolute and relative kidney weights. The female treated dose groups demonstrated increased pigmentation of the renal proximal tubules, however since the pigmentation did not affect the kidney morphology or function, it was not considered a toxic effect. No signs of systemic toxicity were observed in any of the treated groups. The study NOAEL and LOEL was 3 and 12 mg/kg/dy, respectively.

A review of the histopathology from the Eisenbrandt (1987) investigation indicated that combining the number of high dose females with mammary adenomas and adenocarcinomas resulted in a statistically significant increase when compared to controls, however neither category alone was significant. In addition, the incidence of mammary tumors was within the range of the laboratory historical controls and also the control data of the National Toxicology Program. Additional factors indicating that the mammary tumors were not associated with exposure to triclopyr included; the absence of a dose response, no multiple tumors, no early onset and no tumors in males. PATHCO, Inc. reviewed the results of the investigation and also concluded the neoplasms were not related to the administration of triclopyr (Goodman, 1996).

Tsuda (1987) conducted a mouse triclopyr lifetime feeding study using doses of 0, 50, 250 or 1,250 ppm. Results of the 22-month investigation indicated that animals in the high dose group, demonstrated a significant decrease in body weights and a significant increase in male water intake. None of the animals in the study displayed signs of systemic toxicity. Results of urinalysis revealed increased protein and low specific gravity in the high dose females and males, respectively.

Histopathological findings indicated a significant increase in the incidence of distended bladders in the high dose male group. There were no statistically significant increases in compound-related tumors in any of the treatment groups. The female dose groups had an increasing trend of mammary gland adenocarcinomas, however a pair-wise comparisons of the dose groups with the controls demonstrated no statistical significance. The study NOAEL and LOEL was 250 and 1,250 ppm, respectively.

5.13 DEVELOPMENTAL AND REPRODUCTIVE TOXICITY

A review of the triclopyr reproduction and teratology toxicology investigations, did not reveal any evidence that triclopyr has been associated with any significant findings of reproduction dysfunction or teratological effects.

5.13.1 Teratology Studies

Results of a triclopyr rat developmental study demonstrated that signs of maternal toxicity were displayed in the mid and high dose groups animals administered 100 and 300 mg/kg/dy on gestation days 6 through 15. Maternal signs of toxicity were increased salivation, reduced food consumption, decreased weight gain, increased water intake and death in one animal. Kidney weights were slightly increased in the high dose group. The maternal toxicity NOAEL was 30 mg/kg/dy. The offspring from the high dose dams exhibited decreased weight gain, delayed sacrocaudal vertebral arch and cranial centers. There was also an increase in fetuses with unossified sternebrae in the high dose group. The developmental NOAEL was 100 mg/kg/dy (Bryson, 1994a).

A teratology study involving rats dosed with triclopyr at levels of 0, 50, 100 or 200 mg/kg/dy during gestation days 6 through 15 demonstrated signs of maternal toxicity at the two high dose levels as decreased food consumption and body weight gain. The maternal NOAEL was 50 mg/kg/dy. Developmental effects were noted only in the high dose group and consisted of increased resorption rate, slightly decreased fetal body weight and major malformations in 3 fetuses. The triclopyr maternal toxicity and developmental NOAEL for the study were 50 and 100 mg/kg/dy, respectively (Hanley, 1984).

A rabbit triclopyr developmental study involved administering doses of 0, 10, 30 or 100 mg/kg/dy through gestation days 6-18. Animals were sacrificed on day 29. Two maternal deaths occurred in the high dose groups. Signs of maternal toxicity included decreased body weight gain and food intake and higher mean liver and kidney weights. Eight dams aborted their litters. Mid dose animals demonstrated one abortion and early litter delivery in 2 dams. No maternal toxicity was noted in the low dose rabbits. Therefore, the low dose was considered the maternal NOAEL. The Developmental NOAEL for the study was 100 mg/kg/dy (Bryson, 1994b).

5.13.2 Reproduction Studies

Vedula (1995), conducted a 2-generation rat reproduction study with dietary dosing of male and female animals with triclopyr at concentrations of 0, 5, 25 or 250 mg/kg/dy. Following 10 weeks of dietary exposure to the chemical, the first parental (P1) generation was mated to produce the F1 litters. Following weaning, groups of 30 male and 30 female F1 pups were randomly selected to become the second parental (P2) generation. The P2 adults were exposed for 12 weeks and mated to produce the F2 litters.

No adverse treatment-related effects were observed in adult and neonatal males or females in the low dose group. Findings of decreased food consumption and body weights were noted in the high dose group. However, no reproductive or developmental effects occurred in any dose group.

Histologically, the relative kidney weights were increased in the mid and high dose males and only in the high dose females. The kidney appeared to be the target organ for both generations as displayed by degeneration of the proximal tubules. The liver weights were decreased in the high dose groups, but this was not accompanied by any pathological changes. The 5 mg/kg/dy group exhibited no triclopyr-related organ changes throughout the study.

There were no primary treatment-related gross or histopathologic changes of the reproductive organs in either generation of male or female rats in any of the test groups.

Pup adverse health effects included decreased weights, survival and litter sizes in both generations. The fertility and conception rates in both sexes in the high dose group was decreased only in the second generation. The investigators concluded that the parental and fertility/ neonatal toxicity NOAELs were 5 and 25 mg/kg/dy, respectively.

Hanley et al (1984) conducted a 3-generation rat reproduction study administering dietary triclopyr dose levels of 0, 3, 10 or 30 mg/kg/dy. The animals did not exhibit any treatment-related effects regarding reproductive performance, pregnancy parturition or neonatal survival. The investigators concluded that triclopyr had a low potential to adversely affect fetal development or reproductive performance even when the dose levels approached maternal systemic toxicity. The NOAEL for fertility and neonatal toxicity for this study was 30 mg/kg/dy.

5.14 MUTAGENIC EFFECTS

Results of the *in vitro* and *in vivo* triclopyr mutagenesis studies indicate that the chemical is non-mutagenic.

Richold (1979) conducted an Ames assay in Salmonella strains both with and without metabolic activation using rat liver S-9. No significant increase in the number of revertant colonies was observed. Triclopyr was negative in the Ames assay. A similar investigation revealed there was no evidence of growth inhibition for repair competent or deficient bacterial strains either with or without S-9 metabolic activation (Shirasu, 1978).

Results of an *in vivo* dominant lethal study in mice receiving triclopyr doses of 0, 3, l5 and 70 mg/kg/dy/ for 9 weeks was negative (Rao, 1979). Findings from the Rao study were also confirmed by Fabrizio (1973a) in an *in vivo* rat dominant lethal assay. Based on the results of the Rao and Fabrizio investigations, triclopyr is considered not mutagenic in the dominant lethal assay.

A rat *in vitro* unscheduled DNA synthesis (UDS) study was conducted by Mendrala and Dryzga (1986) involving isolated hepatocyte colonies treated with triclopyr and tritiated thymidine. Triclopyr failed to elicit significant UDS at any of the concentrations tested as indicated by a lack of radioactive thymidine concentration in the nucleus of the hepatocytes. Triclopyr's inability to elicit DNA repair indicates an apparent lack of genotoxic activity under the conditions of the assay.

Sibinovic (1973) conducted an acute and subchronic triclopyr host-mediated assay where the chemical was orally administered to mice at dose levels of 0, 0.7 or 70 mg/kg and to a second group of test animals given the same doses daily for 5 days. Three strains of bacteria were injected intraperitoneally, i.p. fluid removed and plated for determination of revertants and recombinants. The findings in the investigation revealed no significant increases in mutant or recombinant frequencies. Triclopyr was considered not mutagenic in the host-mediated assay.

A rat bone marrow chromosomal aberration study demonstrated negative results. The animals were dosed with triclopyr at 0, 0.7, 7 or 70 mg/kg in single dose and repeated 5 day regimens and sacrificed 6, 24 and 48 hours after the last dose. Triclopyr was not considered to be associated with chromosomal aberrations (Fabrizio, 1973b).

Based on the results of the *in vitro* and *in vivo* mutagenic testing, triclopyr is not considered to have significant mutagenic potential.

5.15 CARCINOGENICITY REVIEW

There is no definitive evidence that triclopyr is a carcinogen based on the chemical's toxicology database, findings from the mutagenesis, reproduction and chronic feeding studies.

The carcinogenic potential of triclopyr was evaluated by the EPA Carcinogenicity Peer Review Committee (CPRC). The committee concluded that triclopyr was classed as a Group D chemical (not classifiable as to human carcinogenicity). The committee's decision was based on the increased incidence of mammary tumors in female rats and mice and adrenal pheochromocytomas in male rats in the chronic feeding studies. The majority of the CPRC were of the opinion that the animal evidence provided marginal or not convincing evidence and that the mutagenic findings did not support the chemical being a carcinogen (EPA, 1998).

5.16 EPIDEMIOLOGY REVIEW

A review of the scientific and medical literature provided no citations that any epidemiological investigations concerning triclopyr have been conducted.

5.17 HUMAN CASE REPORTS AND STUDIES

A review of the medical and scientific literature did not provide any substantiated reported cases of human systemic triclopyr poisoning from either ingestion, skin or inhalation exposure to the chemical. The Washington State Department of Health conducts a Pesticide Surveillance Program and have documentation of seven human exposure cases, possibly related to terrestrial use, involving skin and upper respiratory tract irritation following direct exposure to triclopyr spray mist. No signs and symptoms of systemic poisoning were reported, however some of the individuals experienced temporary irritation of the skin and upper respiratory tract. It should be noted that application of the triclopyr product Renovate® Aquatic Herbicide is directly injected under the water and not applied by aerial or spray application (WDOH, 1999).

Triclopyr applicators have the greatest potential to be overexposed to the concentrated formulation. Depending upon the degree and duration of overexposure, dermal and eye contact with triclopyr concentrate may result in moderate and severe skin and eye irritation, respectively. The absence of systemic poisoning associated with triclopyr dermal exposure either in occupational or contact through aquatic herbicidal use is probably due to poor skin penetration of the chemical, huge water dilution factor and low product label use-rates.

Since triclopyr has a very low vapor pressure of 1.26x 10-6 mmHg @25^{o}C, no systemic toxicity, skin or eye irritation or respiratory tract irritation effects are expected from exposure to triclopyr vapor by either applicators or persons contacting treated water (WDOH, 1999).

Should aerial application of concentrated triclopyr occur, overexposure to the spray mist may cause severe irritation to the eyes. However, in the case of eye contact with water treated with triclopyr for aquatic weed control none to minimal eye irritation would result based on the reasons discussed above. Therefore, the WDOH has recommended a 12-hour restriction for re-entry into triclopyr treated water to assure that the eye irritation potential and any other adverse effects will not occur. WDOH also recommends that those wanting to avoid even small exposures can wait 1-2 weeks following application when the triclopyr residues have dissipated from the water and sediments (WDOH, 1999).

5.17.1 Human Neurological Case Reports

There are no reports in the scientific and medical literature listing any findings that either animal or human overexposure to triclopyr has resulted in adverse affects to the central or peripheral nervous systems. The WDOH has not received any reports of neurological effects following exposure to triclopyr spray mist or swallowing of treated water while swimming or in situations where the treated water was used as a drinking water source (WDOH, 1999).

5.17.2 Human Reproduction Case Reports

A review of the triclopyr animal toxicology studies failed to demonstrate any findings of adverse developmental and reproductive effects (Hanley, 1984; Bryson, 1994a,b; Verdula, 1995). Further, no reports were found in the scientific and medical literature associating exposure to triclopyr with any human teratology or reproductive dysfunction.

A review of the medical and scientific literature did not provide any findings or reports that chronic triclopyr exposure occurs when the product is used according to label directions. Subchronic exposure over several days following application of triclopyr would not be expected to result in systemic toxic effects primarily due to the difficulty involved in absorbing a sufficient dose from contacting treated vegetation, soil and water where the chemical is either significantly decomposed, bound or diluted. Secondly, triclopyr is not highly toxic and is poorly absorbed through the skin. Thirdly, the kidneys rapidly eliminate any triclopyr that enters the system.

5.18 EXPOSURE AND RISK ASSESSMENTS

The exposure and risk assessments associated with triclopyr use as an aquatic herbicide are presented in the following Tables, concerning persons engaged in swimming, drinking both potable and treated surface water and eating fish from water where the chemical has been applied. The different types of daily exposures and risk assessments were calculated for both individual and combined scenarios. Based on the estimated triclopyr exposures, the risk assessments were determined by the margins of safety (MOS) and the percent of the reference dose (RfD). The triclopyr calculations were conducted using the label maximum use-rate of 6 pounds Renovate®/ surface acre. The instantaneous triclopyr concentration in the treated water following application is 2.5 ppm or 2.5 mg /Liter or 2.5 ppm. The triclopyr concentration following application decreases to approximately 0.4 ppm by 24 hours and then to 0.1 in 7 days. However, the Allowable Residue Level in Drinking Water (ARLDW) of 500 ug/L was used for exposure calculations beyond 24 hours following application (Dow, 1988; Renovate® label, 1997; Garlon® 3A label, 2000; EPA, 1998).

The calculations presented in the following Tables concerning triclopyr estimated exposures and risk assessments are based on the initial 2.5 ppm triclopyr water concentration, time spent swimming ranging from 0.5 to 3 hours and body weights of 22, 35 and 70 kgs for 6 and 10 year old children and adults, respectively.

Table 2 lists the quantitative toxicology parameters and triclopyr product use-rates that were utilized in conducting the exposure and risk assessments. EPA has determined that the triclopyr RfD is 0.05 mg/kg/dy (50 ug/kg/dy), based on the NOAEL of 5.0 mg/kg/dy finding observed in the 2-generation rat reproduction toxicity study (Verdula, 1995; EPA, 1998) (see Table 4).

The triclopyr dermal parameters of an approximate skin absorption rate of <2 %/24 hours, estimated permeability coefficient and flux rates were used to calculate herbicide dermal exposures from contacting herbicide treated water, see Tables 6-8 (USEPA, 1993; Lunchick, 1994).

Based on the triclopyr maximum use-rates, the exposure estimates and risk assessments were conducted for persons exposed to water containing 2.5 ppm triclopyr for the first 24 hours followed by a water concentration of the chemical of 0.5 ppm or 500 ppb beyond day one. As discussed above, triclopyr continues to decrease below analytical limits of detection following application (Solomon, 1988; Woodburn, 1993a,b; Petty, 1998).

Since triclopyr is applied by subsurface injection for aquatic weed control, it is highly unlikely that any vapor will be generated or drift to expose either applicators or bystanders. For these reasons applicator or bystander triclopyr exposure or risk assessments were not conducted.

Triclopyr is not regulated under the Safe Drinking Water Act and currently does not have a drinking water standard. However, even with the absence of triclopyr drinking water standards, exposure and risk calculations were determined for hypothetical situations involving ingestion and dermal contact with treated water while swimming and drinking potable water. The now expired triclopyr Allowable Residue Level in Drinking Water (ARLDW) of 0.5 ppm or mg/L/day or 500 ug/L/day was used in daily drinking of treated surface water and ingestion of fish from treated water (see Table 3). Although the ARLDW is expired DowAgroscience informed WDOH that EPA decided not to file for an extension because the required label restrictions were deemed sufficiently protective to public health (EPA, 1998; WDOH, 1999). Therefore, the ARLDW of 0.5 ppm has been used for calculations requiring the Maximum Contamination Level (MCL). Based on the assumed water triclopyr concentrations following applications, exposure and risk assessment calculations are presented in the following Tables.

One of the purposes of conducting a review and health risk assessment for use of triclopyr as an aquatic herbicide is to determine whether swimming or contacting water that has been treated according to product label directions, should be a health concern. The situation is discussed in this section and the exposure dose and risk assessment calculations are presented in Tables 5-7.

However, before addressing the exposure to triclopyr treated water, it is important to understand the toxicity classification of undiluted triclopyr according to the results of the acute toxicology studies summarized on Table 1. As indicated in Table 1, the results of the triclopyr product acute oral and dermal animal toxicology studies demonstrate that the chemical is not considered highly toxic and classed in FIFRA Toxicity Categories III and

IV, respectively. A review of Table 1 reveals that one of the most significant findings was that the concentrated triclopyr formulation is classed as a FIFRA Category I eye irritant. The results of the eye irritation studies indicated severe irritation and corneal damage. Section 5.10 discusses how the studies are designed to maximize the eye irritation potential.

One of the reasons for conducting the acute toxicology studies is to provide results for determining the product label signal word warning and precautionary and first-aid statements based on FIFRA toxicity criteria. Thus, the findings from the triclopyr acute toxicology studies dictate the "DANGER" label signal word and the precautionary statements:

> "*DANGER: Corrosive. Causes Irreversible Eye Damage. Harmful if Swallowed or Inhaled. Prolonged or Frequently Repeated Skin Contact with Herbicide Concentrate May Cause an Allergic Skin Reaction in Some Individuals*."

Although the triclopyr products in their undiluted form are severe eye irritants, once the products have been applied to water according to label directions, they become diluted by the water volume, absorb into vegetation, begin degradation and become incorporated into suspended particulate and the sediment. The decrease in the amount of triclopyr in the treated water reduces the amount of chemical available for exposure, thus decreasing the potential for systemic toxicity and eye irritation. The following discussion reviews the triclopyr label dilution use-rate water concentration of 2.5 ppm and the calculated exposure doses and associated health risk assessments to swimmers and others receiving various types of exposure to the aquatically applied herbicide.

The triclopyr product is applied at a prescribed label use-rate in terms of gallons of product/acre of water in order to obtain the specific herbicidal concentration to eradicate the targeted aquatic weed.

The exposure and risk assessment parameters regarding persons swimming in triclopyr treated water are presented in Tables 5-8. Calculation of triclopyr exposures utilized the swimmer's weight (kg), the skin surface area available for exposure (cm2), the amount of time (hours) spent in the treated water containing 2.5 and 0.5 ppm triclopyr, amount of water swallowed while swimming over specific time periods and the estimated human skin permeability coefficient.

Tables 6-8 list the estimated triclopyr oral and dermal exposures and risk assessments for swimmers. The exposure conditions are defined in Table 5. Based on the calculations, it appears that the greatest triclopyr exposure occurs from incidental ingestion of water while swimming. It is estimated that a swimmer swallows approximately 50 ml (nearly 2 ounces) of water/hour (Lunchick, 1994). As listed in Table 8, approximately 96%-99% of triclopyr exposure while swimming occurs through incidental ingestion of water.

A review of Table 6 indicates that even the greatest exposure situation involving the 6 year old group that spends 3 hours swimming in water containing 2.5 ppm triclopyr is well above the MOS of 100 and only receives 34% of the reference dose (RfD) of 50 mg/kg/dy. The MOS and RfD exposure calculations demonstrate significantly increased safety factors for exposure beyond 24 hours.

A review of Tables 7 and 8 reveals that the swimmers' dermal triclopyr exposures are insignificant compared to the oral exposures as supported by the large MOSs and low RfDs.

A review of Table 8 indicates that the dermal route comprises approximately 1%-4% of the total swimmer exposure to triclopyr.

Triclopyr exposure through ingestion and dermal contact with sediment is considered insignificant because of the huge water dilution factor, rapid decomposition and photolysis, adsorption by aquatic plants and incorporation into particulate matter and sediments. The persistence of triclopyr in water is minimal due to these properties. Therefore, exposure to triclopyr from either ingestion or contact with sediments has not been calculated as part of the exposure and health risk assessment evaluation in this document.

Triclopyr has a vapor pressure of 1.26 x 10-6 mmHg @ 25^{o}C. Therefore, any vapor emitted from treated water is considered to be an insignificant route of exposure (Chakrabarti, 1988). No exposure or risk assessments regarding swimmer or bystander exposure to triclopyr vapor from treated water has been included in this document. Since occupational exposure to triclopyr during mixing, loading and applying the chemical is beyond the scope of this document, this route of exposure is not discussed. As mentioned previously, inhalation of triclopyr spray is not considered since the subsurface injection is the major route of application for aquatic weed control.

Table 8 is a compilation of the various types of exposure and total estimated triclopyr doses that a person may receive when swimming in treated water containing either 2.5 or 0.5 ppm of the chemical. The incidental ingestion of water while swimming is the most significant route of exposure. In all cases, approximately 96%-99% of the total triclopyr exposure that occurs while swimming is through the oral route. The same situation as discussed above concerning the exposure and risk assessments for oral exposure to triclopyr while swimming, also applies in the case of the combined chemical exposure where the dose (ug/kg/day) and the MOS and RfD for the 6 year old group swimming for 3 hours in treated water containing 2.5 ppm triclopyr are similarly affected. The MOS and RfD for the same group does not exceed the risk assessment parameters when the triclopyr level decreases to 0.5 ppm beyond 24 hours after application.

At this point, it is important to evaluate any adverse health effects that could potentially be associated with exposure to triclopyr while swimming in treated water. The largest acute exposure (single day exposure) would be expected to occur on the day of the triclopyr product application. Once applied, the concentration of the chemical will decrease to approximately 0.5 ppm beyond 24 hours, thus reducing the daily dose.

Extensive eye contact with water containing 2.5 ppm triclopyr may result in some possible chemical associated temporary minor eye irritation or conjunctivitis. Even eye contact with water not containing triclopyr will result in some minor eye irritation. However, as triclopyr decreases in the water, the potential for minor eye irritation is not considered to be significant.

In summary, it appears that persons swimming in water treated with the highest use-rate of triclopyr of 2.5 ppm are not expected to experience significant adverse health effects. Based on the results of the toxicology studies, the product use-rate, rapid aquatic decomposition, and low systemic toxicity make it unlikely that swimming in recently treated triclopyr water poses a health problem. For example, a 10-year old child would have to drink approximately 3.5 gallons of water containing 2.5 ppm triclopyr during a 3-hour swimming period to obtain a dose equivalent to the NOAEL dose of 3,000 mg/kg/dy (Table 6). Also, some minor eye irritation may be associated with prolonged contact with the 2.5 ppm treated water. However, any redness would remit within a day. The wearing of swim goggles or other eye protection may be useful in avoiding potential minor eye irritation.

Drinking water sources are significant factors in determining the overall exposure to triclopyr, particularly during the first day following application. Table 9 demonstrates that potable drinking water containing the triclopyr ARLDW of 0.5 ppm or 5,000 ug/L does not pose a significant exposure or health risk. The calculations assume daily ingestion of 1-2 liters of water containing 500 ug of triclopyr/L for 6 and 10-year old children. The ARLDW represents the triclopyr concentration in drinking water that is not expected to cause any adverse noncarcinogenic health effects. A 10-year old child would need to drink approximately 35 gallons/day of water containing 500 ug/L triclopyr to obtain the NOAEL systemic toxicity dose of 3,000 mg/kg/dy.

Conversely, Table 10 demonstrates that ingestion of drinking water from treated triclopyr surface water significantly increases the estimated daily exposures and adversely affects the calculated risk assessments. Based on the calculations, ingestion of triclopyr treated water as a daily drinking water source can result in dose levels that exceed the MOSs and RfDs. Nevertheless, as indicated in Table 10, a 10-year old child would require ingestion of approximately 7 gallons of water containing 2500 ug/L triclopyr each day to receive the NOAEL dose of 3,000 mg/kg/dy. Therefore, a 21-day waiting period as indicated on the label is intended to reduce any significant triclopyr exposure.

Consumption of fish taken from triclopyr treated bodies of water appear to be a minor potential dietary source of exposure to the chemical. Hamer (1987) found that triclopyr did not bioconcentrate in bluegill sunfish. However, a report by Carter, 1971 notes the detection of 25 ug/kg in the edible portion of fish. Using Carter’s analytical finding in calculating the exposure doses in Table 11, it does not appear that ingestion of fish from treated water poses any significant health problem or risk.

The total daily-calculated triclopyr exposures are presented in Tables 12 and 13. The difference in the two tables concern potable vs. the triclopyr treated surface water as sources of daily drinking water. Apparently, there are locations that receive residential drinking water directly from treated water sources, e.g. ponds, lakes, and rivers. Since ingestion of water accounts for the greatest potential exposure to triclopyr, both sets of exposure estimates and risk assessments are presented. The total daily exposures listed are the summation of triclopyr daily dose levels received from swimming (Table 8), type of drinking water source (Tables 9 and 10) and ingestion of fish (Table 11).

The findings in Table 12 concerning a summation of the daily estimated triclopyr exposures and risk assessments that include potable water and essentially mimics the calculations presented in Tables 6 and 8. Again, the significant exposures are to the 6-

year old children swimming in 2.5 ppm triclopyr treated water for 2 and 3 hours. However, approximately 24 hours following herbicide application, the 6-year old child swimming for 2 and 3 hours in water containing the ARLDW of 500 ug/L triclopyr does not exceed the total MOS and RfD risk assessment parameters. Since the above discussion is considered a worst case situation, following the WDOH's recommendation that swimming in treated water following 12 hours after application is not expected to result in adverse health effects based on the reduced exposure due to dilution, photolysis, hydrolysis and intake into aquatic vegetation (WDOE, 1999).

Examination of Table 13 reveals a different situation whereby the MOSs and RfDs are exceeded in all age/weight groups. The daily dose levels resulting from ingestion of triclopyr treated surface water at both the 2500 and 500 ug/L concentrations significantly increases the daily triclopyr dose in all subjects and swimming exposure times. Although the calculations represent significantly elevated triclopyr exposures, the doses still remain below the lowest animal chronic toxicology study NOAEL dose of 3,000 ug/kg/dy. Nevertheless, as stated above, it is important to follow the label directions for domestic water use of triclopyr treated water and wait 21 days following application of the chemical before resumption of using the treated water for daily drinking purposes.

5.19 CONCLUSION

Based on a review of the triclopyr chemical and physical properties, use-rates, rapid removal from the aquatic environment by adsorption to particulate, vegetation and sediments, toxicology studies, biotransformation, exposure estimates and risk assessments, it appears that the label directed use of the herbicide for aquatic weed control purposes is not expected to result in any adverse health effects. The exposure evaluation of persons swimming in water containing 2500 and 500 ug/L triclopyr does not indicate that adverse systemic health effects would occur based on the exposure and risk assessment parameters. Aside from 6-year olds drinking immediately treated surface water as part of their daily diet, the only other risk assessment exceeded involved the same age group swimming for 2 and 3 hours in water containing 2500 ug/L triclopyr and drinking dietary potable water containing 500 ug/L (Table 12). Even though the risk assessment was exceeded, the potential daily triclopyr dose calculates to approximately 73-87 times less than the systemic MOS based on the animal chronic toxicology NOAEL of 3,000 ug/kg/day. Although the systemic toxicity MOS was exceeded in the above exposure scenario, the RfD remained below 100%.

Risk assessments were significantly exceeded in situations where the source of drinking water involved ingestion of triclopyr from immediately treated water. Although the calculated triclopyr daily doses were elevated, they remained 26-42 times below the systemic animal chronic toxicology NOAEL. Again, it is important to follow the triclopyr product label that recommends waiting 21 days before resuming use of treated water as a drinking water source.

Based on the label use directions and the results of the triclopyr toxicology studies, the aggregate or combined daily exposure to the chemical from aquatic herbicidal weed control does not pose an adverse health concern.

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LIST OF TABLES

Table 1: Triclopyr Acute Toxicology

Study	Results	Toxicity Category	Reference
Acute Oral Rats	LD50 Male = 2,574 mg/kg Female = 1,847 mg/kg	III	Mizell, 1988(a)
Acute Dermal Rabbits	LD 50 = >5,000 mg/kg	IV	Gilbert, 1996
Acute Inhalation Rats	LC50 = 2.6 mg/l	IV	Nitschke, 1989
Skin Irritation Rabbits	Non-Irritating	IV	Mizell, 1988(b)
Eye Irritation Rabbits	Severe Irritation and Damage	I	Mizell, 1988(c)
1:3 Dilution – Rabbits	Eyes Normal by Day 7		Henck, 1980(a)
1:7 Dilution – Rabbits	Eyes Normal by 24-hours		Henck, 1980(b)
Skin Sensitization	Skin Sensitizer in Guinea Pigs		Mizell, 1989 Berdasco, 1994

Table 2: Triclopyr Toxicology Quantitative Parameters

Regulatory Guideline	**Standard/Dose (mg/kg/dy)**	**Reference**
Toxicology		
Subchronic NOEL	5.0 mg/kg/dy (90 dys)	(Landry, 1984)
Chronic NOEL - Rat	3.0 mg/kg/dy	(Eisenbrandt, 1987)
Chronic RfD	0.05 mg/kg/dy or 50.0 ug/kg/dy	(EPA, 1998)
Reproduction NOEL - Rat	5.0 mg/kg/dy	(Verdula, 1995)
Cancer Classification		
EPA	Group D (not classifiable as to human carcinogenicity)	
IARC	Not Evaluated	
Dermal		
Absorption = ~1.6%/ 96-hours - Human (Carmichael, 1988)		
Estimated Permeability Coefficient = 1 x 10-4 cm/hr		
Estimated Flux Rate (2.5 ppm use-rate) = 2.5 x 10-4 $mg/cm^2/hr$		
Inhalation		
Dow Industrial Hygiene Guideline (IHG) = 2 mg/M^3 (Garlon® 3, MSDS, 9/9/99)		
No American Conference of Governmental Hygienists Threshold Limit Value (TLV) Established (ACGIH, 1997).		
Triclopyr Label Use-Rates		
Renovate® Aquatic Herbicide Contains 3 pounds triclopyr acid equivalent/gallon = 6 pounds triclopyr acid equivalent / surface acre = 2.5 parts per million (ppm) or (mg/L) or (ug/ml) as immediate water concentrations of triclopyr acid equivalent		

Table 3: Triclopyr Health Advisories

Drinking Water	
ARLDW[a]	0.50 mg/L or 500 ug/L
MCLG[b]	NA
MCL[c]	NA
DWEL[d]	NA
1 day HA[e]	NA
10 day HA[f]	NA
Longer term HA[g]	NA
Tolerance Potable Water	NA
Dietary ADI	NA
Tolerance	
Cattle, Goats, Hogs, Horses and Sheep: Meat, Fat and Meat Byproducts = 0.05 ppm Liver and Kidney = 0.5 ppm	
Poultry: Meat, Fat and Meat Byproducts (except Kidney) = 0.1 ppm	
Milk = 0.01 ppm	
Fish and Shellfish = 0.2 ppm (expired 6/30/00)	
Registered for Use on Rice Rice Grain Tolerance = 0.3 ppm Rice Straw Tolerance = 10 ppm	

a. Allowable Residue Level in Drinking Water – A temporary triclopyr concentration in potable water expected to be protective of adverse human health effects. Triclopyr is not regulated under the Safe Drinking Water Act.

b. Maximum Contamination Level Goal – A non-enforceable concentration of a drinking water contamination that is protective of adverse human health effects and allows an adequate MOS.

c. Maximum Contamination Level – Not established for triclopyr. Tryiclopyr not regulated under the Safe Drinking Water Act.

d. Drinking Water Equivalent Level – A lifetime exposure concentration protective of adverse, noncancer health effects, that assumes all of the exposure to a contaminant that is from a drinking water source.

e. One-day health advisory – concentration of a chemical in drinking water that is not expected to cause any adverse non carcinogenic effects for up to 5 consecutive days of exposure, with a MOS.

f. Ten-day health advisory – same as one day HA for up to 14 consecutive days of exposure, with MOS

g. Longer Term health advisory – same as one day HA for up to 7 years (10% of lifetime of exposure) consecutive exposure, with MOS.

Reference: USEPA, 1998

Table 4: Triclopyr Risk Assessment Noncarcinogenic Parameters

Effect	Study	NOEL	LEL	Reference
Systemic Toxicity	Chronic: 2-Yr Rat Dietary Doses: 0, 3, 12 or 36 mg/kg/dy	3 mg/kg/dy or 3,000 ug/kg/dy	12 mg/kg/dy	Eisenbrandt, 1987
Reproduction Toxicology	Rat 2-Generation Dietary Doses: 0, 5, 25 or 250 mg/kg/dy	5.0 mg/kg/dy or 5,000 ug/kg/dy	25 mg/kg/dy	Verdula, 1995
Teratology	Rabbits dosed on days 6-18 of gestation Doses: 0, 10, 30 or 100 mg/kg/dy	Developmental effects 100 mg/kg/dy Maternal toxicity 10 mg/kg/dy	30 mat tox >100 devel	Bryson, 1994b

Table 5: Swimming: Triclopyr Aquatic Exposure and Risk Assessment Parameters

Subjects

Age	**Weight (kg)**	**Pounds**	**Body Surface Area (cm^2)**
6 years	22	48	8,800
10 years	35	77	12,000
Adult	70	154	18,000

Water Exposure Time (Hours)

0.5
1.0
2.0
3.0

Amount Of Water Ingested During Swimming

25 ml/0.5 hours
50 ml/ l hour
100 ml/ 2 hours
150 ml/ 3 hours

Triclopyr Constants

Maximum use-rate = 2.5 ppm or 2.5 mg/L of water (Renovate® label, 1997)
or 2,500 ug/L or 2.5 ug/ml
Typical use rate = 2.5 ppm
Estimated Permeability Coefficient (skin) = 1×10^{-4} cm/hr
Octanol/Water Partition Coefficient = NA[1]
Vapor pressure = 1.26 x 10-6 mmHg @ 25^{o}C (Chakrabarti, 1988)
Water Solubility = 440 mg/L @ 25^{o}C (The Merck Index, 1989)

Aquatic Environmental Fate

Triethylamine salt active ingredient in Renovate® rapidly hydrolysis to triclopyr acid following aquatic application. Triclopyr acid undergoes photolysis into 3,5,6-trichloro-2-pyridinol (TCP) and 3,4,5-trichloro-2-methoxypridine (TMP). TCP and TMP are further degraded by photolysis and biotransformation. The half-life for triclopyr is determined to be 3.6 – 4.7 days (Solomon, 1988; Woodburn, 1993; Petty, 1998).

[1] NA = Not available

Table 6: Swimming: Triclopyr Oral Exposure And Risk Assessment[a]

Age (yrs)	Wt (kg)	Exposure Time (hrs)	Water Ingested (mls)	Triclopyr Total Exposure[a] (ugs)	Daily Oral Dose[b] (ug/ml/kg)	Margin of Safety		%RfD (ug/kg/dy)
						Systemic 3,000 ug/kg/dy	Repro[c] 5,000 ug/kg/dy	
2.5 ppm use-rate or 2500 ug/L or 2.5 ug/ml								
6	22	0.5	25	63	2.8	1,071	1,786	6
		1.0	50	125	5.7	526	877	11
		2.0	100	250	11.4	263	439	23
		3[d]	150	375	17	176	294	34
10	35	0.5	25	63	1.8	1,667	2,778	4
		1.0	50	125	3.8	789	1,316	7
		2.0	100	250	7.0	429	714	14
			150	375	10.7	280	467	21
Adults	70	0.5	25	63	0.9	3,333	5,555	2
		1.0	50	125	1.8	1,667	2,778	4
		2.0	100	250	3.6	833	1,389	7
		3.0	150	375	5.3	566	943	11
0.5 ppm ARLDW or 500 ug/L or 0.5 ug/L								
6	22	0.5	25	13	0.6	5,000	[c]	1
		1.0	50	25	1.0	3,000		2
		2.0	100	50	2.3	1,300		4.6
		3.0	150	75	3.4	822		7.0

Table 6: Swimming: Triclopyr Oral Exposure And Risk Assessment[a] (Continued)

Age (yrs)	Wt (kg)	Exposure Time (hrs)	Water Ingested (mls)	Triclopyr Total Exposure[a] (ugs)	Daily Oral Dose (ug/ml/kg)[b]	Margin of Safety		%RfD (ug/kg/dy)
						Systemic 3,000 ug/kg/dy	Repro[c] 5,000ug/kg/dy	
10	35	0.5	25	13	0.4	7,500		0.8
		1.0	50	25	0.7	4286		1.4
		2.0	100	50	1.4	2,143		3
		3.0	150	75	2.0	1,500		4
Adult	70	0.5	25	13	0.17	17,650		0.3
		1.0	50	25	0.36	8,333		0.7
		2.0	100	50	0.7	4,280		1.4
		3.0	150	75	1.0	3,000		2

[a] Oral Exposure = Exposure Time (hrs) X 50 ml (water ingested/hr) X Triclopyr water con. (ppm)

[b] Oral Dose = Oral Exposure (ug/dy) / Body Wt (kg) = ug/kg/day

[c] Due to large MOSs for Systemic Toxicity, no MOSs calculated for Reproduction Toxicity

[d] Ingestion of ~7 gallons of water containing 2.5 ppm triclopyr during 3 hrs swimming required to equal systemic NOAEL dose of 3,000 ug/kg/dy

Table 7: Swimming: Triclopyr Dermal Exposure and Risk Assessment[a]

Dermal Exposure (ug/day) = Exposure time (hrs) x SA x Flux Rate
Dermal Dose (ug/kg/dy) = Dermal Exposure / Body Weight (kg)
ET = Exposure Time (0.5, 1.0, 2.0 or 3.0 hours swimming/day)
SA = Total Body Surface Area (cm^2)
Estimated Permeability Coefficient = 1×10^{-4} cm/hr
Flux Rate = Permeability Coefficient x Triclopyr Water Concentration
(1.0×10^{-4}) x 2.5 ppb or ug/ml = 2.5×10^{-4} ug/cm^2/hr)
TDD = Total Daily Triclopyr Exposure / Body Weight (expressed below in ug/kg/day)
BW = Body Weight (kg)

Age (yrs)	**Wt (kg)**	**Exposure Time (hrs)**	**Body Surface Area (cm^2)**	**Flux Rate**	**Dose/Day Dermal (ug/kg/day)**	**Margin of Safety**	
						Systemic 3,000 ug/kg/dy	**Repro Tox 5,000ug/kg/dy**
2.5 ppm use-rate or 2500 ug/L or 2.5 ug/ml							
6	22	0.5	8,800	2.5×10^{-4}	0.05	60,000	[b]
		1.0			0.1	30,000	
		2.0			0.2	15,000	
		3.0			0.3	10,000	
10	35	0.5	12,000	2.5×10^{-4}	0.043	69,800	
		1.0			0.086	34,900	
		2.0			0.17	17,600	
		3.0			0.26	11,500	
Adult	70	0.5	18,000	2.5×10^{-4}	0.032	93,800	
		1.0			0.064	46,900	
		2.0			0.13	23,100	
		3.0			0.19	2,222	

[a] Due to the low amounts of the triclopyr dermal doses calculated for the 2.5 ppm use-rate, no calculations were conducted to determine doses at the ARLDW of 500 ug/L.

[b] No calculations for reproduction toxicity MOSs because of large systemic NOAELs.

Table 8: Swimming: Triclopyr Total Exposure and Assessment

TOTAL TRICLOPYR EXPOSURE= Total Oral + Total Dermal (ug/kg/dy)

Age	Wt	Exp. Time	Oral (ug/kg/dy)	[% tot exp]	Dermal (ug/kg/dy)	Total (ug/kg/dy)	Margin of Safety		%RfD (ug/kg/dy)
							3,000 ug/kg/dy	5,000ug/kg/dy	
2.5 ppm or 2500 or 2.5 ug/L max use-rate									
6	22	0.5	2.8	98	0.05	2.85	1,053	[a]	6
		1.0	5.7	98	0.1	5.80	517		9
		2.0	11.4	98	0.2	11.6	257		9
		3.0[b]	17	98	0.3	17.3	173		35
10	35	0.5	1.8	98	0.04	1.84	1,630		4
		1.0	3.8	97	0.09	3.9	769		8
		2.0	7.0	97	0.17	7.2	417		14
		3.0	10.7	97	0.26	11	273		22
Adult	70	0.5	0.9	97	0.032	0.93	3,226		2
		1.0	1.8	96	0.064	1.87	1,604		4
		2.0	3.6	97	0.13	3.7	811		7
		3.0	5.3	96	0.19	5.5	545		11
ARLDW = 0.5 ppm or 500 ug/L or 0.5 ppb									
6	22	0.5	0.57	98	0.01	0.57	5,263		1
		1.0	1.1	99	0.01	1.1	2,727		2
		2.0	2.3	98	0.03	2.3	1,304		5
		3.0	3.4	99	0.04	3.4	822		7

[a] Due to high NOAEL for reproduction toxicity, MOSs not calculated.

[b] Requires ingestion of approximately 7 gallons of water containing 2500 ug triclopyr/L during 3 hours swimming to equal the systemic NOAEL of 3,000 ug/kg/day.

Table 9: Triclopyr Exposure and Risk Assessment Drinking Potable Water

PARAMETERS:

Allowable Residue Level in Drinking Water (ARLDW) = 0.5 mg triclopyr / L water
= 500 ug/L or 0.5 ug/ml
Drinking Water Intake/Day

6 year old = 1000 ml or 1.0 liters
10 " " = 1000 ml or 1.0 liters
Adult = 2000 ml or 2.0 liters

Age	**Wt**	**Triclopyr Exposure (ug)**	**Water Dose (ug/kg/dy)**	**Margin of Safety**		**% RfD**
				Systemic 3,000 ug/kg/dy	**Repro Tox 5,000 ug/kg/dy**	
6	22	500	23	131[a]	217	46
10	35	500	14	214	357	28
Adult	70	1,000	14	214	357	28

[a] A 22 kg child needs to daily drink approximately 35 gallons of water containing the ARLDW 500 ug/L triclopyr to equal the systemic NOAEL of 3,000 ug/kg/dy.

Table 10: Triclopyr Exposure and Risk Assessment Drinking Treated Surface Water

ORAL EXPOSURE (OE) = IR x WC

ORAL DOSE (OD) = OE / BW

OE = Oral Exposure (ug/day)
IR = Ingestion Rate (6 and 10 year olds 1 liter/day; adult 2 liters/day)
WC = Water Concentration (2.5 and 0.4 ppb or ug/ml)
OD = Oral Dose (ug/kg/dy)
BW = Body Weight (kg)

Age (yrs)	Wt (kg)	IR (L/dy)	OE (ug/dy)	OD (ug/kg/dy)	Margin of Safety		%RfD (ug/kg/dy)
					3,000 ug/kg/dy	5,000 ug/kg/dy	
2.5 ppm or 2500 ug/L or 2.5 ppb or ug/ml Max Use-Rate							
6	22[a]	1	2,500	114	26	44	228
10	35	1	2,500	236	12	21	472
Adult	70	2	5,000	236	12	21	472
0.5 ppm ARLDW = 5,000 ug/L or 0.5 ppb or ug/ml							
6	22	1	500	23	131	217	46
10	35	1	500	14	214	357	28
Adult	70	2	1,000	14	214	357	28
0.125 ppm 14 Days Post-Application[b]							
6	22	1	125	5.7	526	877	11
10	35	1	125	3.6	833	1,389	7
Adult	70	2	20	3.6	833	1,389	7

[a] A 22 kg child needs to drink approximately 7 gallons of triclopyr treated water containing 2.5 ug/L each day to equal the systemic toxicity NOAEL of 3,000 ug/kg/dy.

[b] Estimated triclopyr water concentration 14 days following maximum application use rate. Estimate based on 95% triclopyr dissipation in water (Woodburn, 1993; Solomon, 1988; Getsinger, 1997; Petty, 1998; WDOH, 2000).

Table 11: Triclopyr Exposure And Risk Assessment Ingestion Of Fish

Triclopyr does not bioconcentrate in edible tissue of fish.
Typical analytical level detected in fish from recently treated water has been reported to contain 0.2 ppm or mg/kg or 200 ug/kg (Petty, 1998)
Human fish consumption (USEPA, 1989):

70 kg person fish intake/meal = 0.4 kg
35 “ “ “ “ = 0.2 kg
10 “ “ “ “ = 0.06 kg

Age	**Wt**	**Fish Meal Wt (kg)**	**Triclopyr Exposure (ug)**	**Dose ug/kg/dy**	**Margin of Safety**		**%RfD**
					Systemic 3,000 ug/kg/dy	**Repro Tox 5,000 ug/kg/dy**	
6	22	0.06	12	0.5	6,000	10,000	1.0
10	35	0.2	40	1.1	2,727	4,454	2.0
Adult	70	0.4	80	1.1	2,727	4,454	2.0

Table 12: Triclopyr: Total Calculated Daily Exposure and Risk Assessment Drinking Potable Water

Age	Wt	Exposure Time (hrs)	Swim Dose (ug/kg/dy)	Water Dose[a] (ug/kg/dy)	Fish Dose (ug/kg/dy)	Total Dose (ug/kg/dy)	Margin of Safety		%RfD (ug/kg/dy)
							Systemic 3,000 ug/kg/dy	Repro Tox 5,000 ug/kg/dy	
0.5 ppm or 500 ug/L or 0.5 ppb ARLDW									
6	22	0.5	2.85	23	0.5	26.4	114	189	53
		1.0	5.8	“	“	29.3	102	171	59
		2.0	11.6	“	“	35	87	143	70
		3.0	17.3	“	“	41	73	122	82
10	35	0.5	1.84	14	1.1	17	176	294	34
		1.0	3.9	“	“	19	158	263	38
		2.0	7.2	“	“	23	130	217	46
		3.0	11	“	“	26	115	192	52
Adult	70	0.5	0.93	14	1.1	16	188	313	32
		1.0	1.87	“	“	17	176	294	34
		2.0	3.7	“	“	19	158	263	38
		3.0	5.5	“	“	27	111	185	54

[a] Represents triclopyr exposure from potable drinking water (ARLDW = 500 ug/L)

Table 13: Triclopyr: Total Calculated Daily Exposure and Risk Assessment Drinking Treated Surface Water

Age	Wt	Exposure Time (hrs)	Swim Dose (ug/kg/dy)	Water Dose[a] (ug/kg/dy)	Fish Dose (ug/kg/dy)	Total Dose (ug/kg/dy)	Margin of Safety		%RfD (ug/kg/dy)
							Systemic 3,000 ug/kg/dy	Repro Tox 5,000 ug/kg/dy	
2.5 ppm or 2,500 ug/L or 2.5 ppb or ug/ml Max Use-Rate									
6	22	0.5	2.85	114	0.5	114	26	44	228
		1.0	5.80	“	“	115	26	43	230
		2.0	11.6	“	“	116	26	43	232
		3.0	17.3	“	“	117	26	43	234
10	35	0.5	1.84	71	1.1	71	42	70	144
		1.0	3.9	“	“	72	42	69	144
		2.0	7.2	“	“	72	42	69	146
		3.00	11.0	“	“	73	42	68	146
Adult	70	0.5	0.93	71	1.1	71	42	70	142
		1.0	1.87	“	“	71	42	70	142
		2.0	3.7	“	“	72	42	69	144
		3.0	5.5	“	“	72	42	69	144
0.5 ppm or 500 ug/L or 0.5 ppb or ug/ml ARLDW									
6	22	0.5	0.57	23	0.5	24	125	208	48
		1.0	1.1	“	“	24.6	122	203	49
		2.0	2.3	“	“	26	115	192	52
		3.0	3.4	“	“	27	111	185	54

[a] Represents triclopyr exposure from drinking treated surface water