#### Triclopyr Questions and Answers

These questions were submitted by the public. The questions were answered by a team of experts.

## 1. What is triclopyr?

Triclopyr (*pronounced tri–clo–peer*) is an herbicide that can control infestations of Eurasian watermilfoil and other broad-leaf water plants. Eurasian watermilfoil is more sensitive to triclopyr than many native aquatic species including coontail, rushes and cattails. Triclopyr can therefore be used at label concentrations to remove Eurasian watermilfoil without killing many native plants. One triclopyr product is currently registered and marketed for aquatic weeds - Renovate 3<sup>TM</sup>.

# 2. There are two types of triclopyr. Which one is registered for aquatic use? What distinguishes these two types of triclopyr from each other?

Renovate  $3^{TM}$  (triethylamine salt of triclopyr – 3 lb/gal acid equivalent) is the only formulation of triclopyr registered by the US EPA as an aquatic herbicide. The other formulation Garlon 4 is a butoxyethyl ester formulation with 4 lb/gal acid equivalent and this formulation is not registered for aquatic use.

### 3. Has a full risk assessment been performed on triclopyr? If so, by whom?

An Environmental Impact Statement (EIS) has been completed by the Washington Department of Ecology and a full risk assessment was conducted by Ecology and formed the basis for the EIS.

#### 4. How toxic is triclopyr to humans?

Concentrated triclopyr products are corrosive and can cause skin irritation and irreversible eye damage if splashed in the eye. However, only dilute amounts of triclopyr are needed to kill Eurasian watermilfoil. These dilute concentrations have not been shown to cause skin irritation or other health effects. Triclopyr is not well absorbed through skin. If ingested, research has shown that low doses of triclopyr are rapidly excreted in humans and are unlikely to accumulate in human tissue or cause adverse effects.

In natural waters, the initial breakdown products of triclopyr are TCP and TMP. Tests in laboratory animals on both these metabolites have shown that their toxicity to mammals is less than or equal to triclopyr. These metabolites are relatively shortlived in the environment. Complete breakdown of triclopyr results in carbon dioxide, oxamic acid, and other low molecular weight carboxylic acids.

Triclopyr is not considered to be a cause of cancer, birth defects, or genetic mutations. Nor is it considered likely to cause systemic, reproductive, or

developmental effects in mammals at or near concentrations encountered during normal human use. However, Washington State Department of Health considers it prudent public health advice to minimize exposure to pesticides regardless of their known toxicity.

#### 5. Does triclopyr accumulate in human and animals?

Triclopyr and its metabolites are excreted rapidly in humans and mammals. A study in human volunteers, given low doses showed that blood levels peaked two to three hours after ingestion and declined to undetectable levels within 48 hrs. A studies in rodents showed that triclopyr and metabolites have a short residence time in other bodily tissues (12-15 hours).

### 6. Is there any relationship between triclopyr and cancer?

Triclopyr was determined to be "not classifiable as to human carcinogenicity" by EPA reviewers. This means the EPA did not consider the animal evidence to be sufficient to list triclopyr as a possible human carcinogen. Nor did it find the evidence definitive enough to rule out carcinogenicity. EPA considered results of the a 22 month assay in mice, a 24 month assay in rat, and results from *in vitro* tests for mutations. There were marginal increases in some breast tumors (benign) but no consistent pattern across dose groups and no dose-response pattern. EPA does not consider this a data gap since the required studies were conducted and were acceptable to EPA.

## 7. Does triclopyr have impacts on reproduction?

EPA requires that pesticides be assessed for reproductive effects. In the reproductive tests two generations of rodents are fed the pesticide in their daily diet. It is common that pesticides have a positive response at the highest dose tested. This is because the test protocol requires the highest dose to be high enough to elicit a reproductive effect (unless the dose required causes death or severe suffering of the animal). Generally the highest dose must show an effect or the test is unacceptable to EPA. Impairment of reproduction by triclopyr was seen only at doses high enough to cause toxicity to the mothers. No reproductive effects were seen at lower doses. The high dose was very high relative to potential human exposure. It was 500 times the dose considered by EPA to be safe for daily exposure to humans and over 1400 times higher than the worst-case scenario for human exposure to triclopyr in lake treatments.

# 8. At what levels of application is there documented evidence of impacts to people, fish, wildlife, microorganisms etc? Will these levels be achieved in applications to lakes to control Eurasian watermilfoil?

Renovate 3<sup>TM</sup> is used at levels no greater than 2.5 ppm (maximum labeled rate) in lakes. These levels have been found to be safe to the environment and non-target species based upon testing conducted for US EPA Registration.

#### 9. If my lake is treated with triclopyr, will I be exposed to this herbicide?

Residues of triclopyr and its metabolites should not be detectable in lake water more than a couple weeks past the application. If you do wade or swim in the lake, touch pets that have been in the lake, or eat fish from treated water shortly after the treatment, you may be exposed to dilute concentrations of triclopyr and its metabolites.

There is little chance of exposure to bystanders during the herbicide application process. This is because liquid triclopyr herbicide is injected directly into the water column. The application method eliminates opportunity for drift of sprays onto bystanders or nearby residents during the application. Triclopyr has a low vapor pressure and is quite water-soluble so it will not volatilize from treated water and drift through air following the application.

#### 10. Is it safe to swim or play in the water following the herbicide application?

There are no swimming restrictions on the Renovate 3<sup>™</sup> label following application of triclopyr to water. This means that the federal EPA considers the treated water safe for swimming. However, to impose an additional layer of safety to swimmers (due to potential for eye irritation) the Washington Department of Ecology is imposing a twelve hour swimming restriction in Washington after treatment with triclopyr.

Washington State Department of Ecology recently contracted for an independent scientific assessment of triclopyr safety including this question of a swimmer's exposure. The most conservative scenario considered was a six-year-old who swims for three hours and inadvertently swallows 150 ml of water from a lake treated with the maximum allowable rate of triclopyr. The estimated amount the child would absorb in this scenario was still more than 100 times less than the daily dose animals were fed over their lifetime with no observable adverse effects.

Washington State Department of Health (DOH) has reviewed the data and agrees that skin contact with treated water at the dilute treatment concentration is unlikely to result in any adverse health effect in people. Triclopyr products are concentrated when initially injected into water during an application so, as a precaution, DOH advises people to avoid contact with water in treated areas for twelve hours following an application to allow the herbicide concentrate to disperse and reach the dilute treatment concentration.

#### 11. Are fish from the treated area safe to eat?

One breakdown product of triclopyr, called TMP, can temporarily accumulate in fish and shellfish immediately following a triclopyr application. The EPA did not consider the concentration of this metabolite to be of health concern and requires no fishing restrictions.

Washington State Department of Ecology recently contracted for an independent scientific assessment of triclopyr safety including this question of eating fish from treated

waters. Scenarios for children and adults consuming fish every day from treated water resulted in estimated exposures that were more than 1000 times less than the daily doses animals were fed over their lifetime with no observable adverse effects.

### 12. Has triclopyr been tested for special sensitivity to children?

The EPA is required to assess each pesticide for its potential to cause toxicity specifically to infants and young children. This is because children's bodies are still developing and they may be more susceptible to the action of a toxicant. EPA conducted this assessment using animal tests and concluded "Reliable pre-and post-natal data indicate no special sensitivity of young animals to triclopyr residues."

### 13. What are the toxicity levels of triclopyr to aquatic organisms?

For aquatic organisms, the acute toxicity values for triclopyr with rainbow trout, salmon species, bluegill sunfish, and the water flea (*D. magna*) are shown below in Text Table 1. <u>Note</u>: All testing done with laboratory water at pH of  $\sim$ 7-8, typical of conditions in the Pacific NW area, as demonstrated in Figure 1.



Figure 1. Surface water pH for Puget Sound tributaries (from U.S. Geological Survey)

Text Table 1. Acute toxicity data for aquatic species with Triclopyr

	R. Trout	Salmon sp.	Bluegill	Water Flea
Acute 96-hr LC50 (ppm)	86 to 117	82 to 182	148	133 (48-hr)
EPA Toxicity Rating: "Sligl	ntly toxic to Pr	actically non-to	xic"	

The EPA classifies pesticides according to their acute toxicity responses. Compounds with acute values >100 ppm are classified "Practically non-toxic" (best rating), while compounds with acute values of 10-100 ppm are classified as "Slightly toxic" (second best classification). The overall weight of evidence indicates that triclopyr acute toxicity values average ~100 mg/L or greater with invertebrate and vertebrate species, indicating

that a collective "Practically non-toxic" rating is most appropriate as a generic classification.

# 14. What does "practically non-toxic" mean?

chemicals. In the chart below you will see that it is the lowest toxicological category.							
Table II: Ecotoxicological Categories							
Toxicity Category	Mammalian (Acute Oral)* mg/kg	Avian (Acute Oral)* mg/kg	Avian (Dietary)- ppm	Aquatic Organisms <sup>‡</sup> ppm			
very highly toxic	<10	<10	<50	<0.1			
highly toxic	10-50	10-50	50-500	0.1-1			
moderately toxic	51-500	51-500	501-1000	>1-10			
slightly toxic	501-2000	501-2000	1000-5000	>10-100			
practically non-toxic	>2000	>2000	>5000	>100			

Practically non-toxic is an ecotoxicological category used to describe pesticides and other chemicals. In the chart below you will see that it is the lowest toxicological category.

\* Reflects dose given to test animals and is based on body weight of the test animal. \_Concentration in the diet. Unrelated to body weight of the test animal. Measure of environmental exposure.

‡Concentration in water. Unrelated to body weight of test animal. Measure of environmental exposure.

The words "pesticide" and "poison" are not synonymous. Relatively few pesticides are poisonous to humans according to the standard meaning of the term. "The dose makes the poison" is a saying all doctors understand. What it means, in essence, is that it's not simply *what* you come in contact with or ingest that determines risk, it's also *how much* you contact or ingest. This point is important because most pesticides are designed to control pests with amounts far smaller than the amount that would affect humans and pets. Contrary to popular belief, pesticides are not a uniquely toxic class of substances. They range from practically non-toxic to highly toxic—as with other classes of natural and manmade substances.

# 15. Why does the Renovate 3<sup>™</sup> label state to not apply to saltwater? Does it become toxic in a saltwater environment? Are salt water plants, creatures etc more susceptible to triclopyr than freshwater? If so how and why?

A pesticide can only be directly applied to sites that it has been approved for through the US EPA label registration process. The label only indicates where a pesticide may be applied and does not restrict where residues may be discharged. Triclopyr does not become toxic in salt water. Salt water plants and animals should not be any more sensitive to triclopyr than the freshwater organisms that have been tested with triclopyr. As an example from the Renovate 3<sup>TM</sup> Material Safety Date Sheet (MSDS) the Acute

LC50 for pink shrimp (*Penaeus duorarum*) is 895 mg/L. This is over 350 times higher than the maximum rate that is normally applied to lakes.

# 16. What are the long term affects of triclopyr on mammal systems - if it accumulated in mammalian tissue 5 yr, 10 yr, 20 yr. later?

Populations of several native mammals and birds were studied for several years following triclopyr, prescribed burning, and combination treatments in oak-savanna woodlands. Populations for all species showed either no change or increases following treatments. Thymus gland weights showed a statistically significant increase in burned areas both with and without triclopyr applications (Lochmiller et al. 1995). Recently published studies showed no impact of triclopyr applications on wildlife populations, relative to non-herbicide based vegetation management practices (Duchesne et al. 1999; Harpole and Haas 1999; Leslie et al. 1996; Leutenschlager et al. 1998; Lindgren et al. 1998; Nolte and Fulbright 1997). One study (Obenshain et al. 1997) reports that the combined use of triclopyr with 2,4-D and glyphosate may lead to concentrations of these herbicides in water that may cause adverse effects which are not detailed in the publication. In mammals, most triclopyr is excreted, unchanged, in the urine. Triclopyr was observed to concentrate slightly in ovaries of laboratory animals given repeated doses. No accumulation was observed in other tissues. The authors concluded that triclopyr and its metabolites are likely to have a low potential to accumulate upon repeated exposure (Timchalk et al. 1990). Data quoted from this website: http://www.fs.fed.us/r6/weeds/Triclopyr Profile.PDF

# 17. Could triclopyr possibly impact bats and or other mammals, especially bats that are pregnant or nursing their young?

Renovate3<sup>TM</sup> has a low potential for bioaccumulation. Triclopyr is typically found at a concentration in animals many times less than what is present within the surrounding water and is eliminated relatively quickly. The LD50 for Rats has ranged from 630-729 mg/Kg (Tu et. al.). Since the material does not bioaccumulate bats would not be able to develop concentrations that would affect them or their offspring by drinking treated water or foraging on insects from the treated water.

## 18. What are the inert ingredients in triclopyr?

Garlon 3A<sup>TM</sup> and Renovate 3<sup>TM</sup> are identical products marketed under two names. Ingredients listed on either the pesticide label or Material Safety Data Sheet are:

- triclopyr TEA salt (44.4%)
- ethanol (amount not specified but more than 1%)
- triethylamine 3%,
- ethylenediamine tetraacetic acid 2.3%.

The regulatory manager at Dow Agrosciences (manufacturer of triclopyr) disclosed that the product is more than 45% water and contains small amounts of an antifoam product

and a surfactant. He explained that triethylamine is used extensively in cosmetics and has an allowable level in food. He also explained that EDTA helps the product adjust to the hardness of the lake water. He confirmed that the ethanol was present at ~2% of the formulated product. Some of the other ingredients could contribute to the hazard of the product for pesticide applicators if direct skin or eye contact with the concentrated product occurs. The other ingredients listed do not pose a risk to the general public in contact with the diluted product. This is because the product is diluted in water more than 100,000–fold for control of Eurasian watermilfoil.

# 19. Are there "gaps" in the data on triclopyr - things that we do not know the answers to?

There are often site-specific endangered animals or rare plants that have not been tested. To avoid impacts, the Washington Department of Ecology requires that the applicant check with the Department of Natural Resource's Heritage Program for rare plant locations and to consult the lists for animals. Because some salmon stocks are listed as threatened and endangered in the Pacific Northwest, the Washington Department of Ecology has also contracted with the University of Washington to conduct tests for potential sub-lethal effects on salmon with various herbicides.

#### 20. Are there any "unknown" risks to the use of triclopyr?

The world is full of potentially toxic substances and dangerous situations. However, separating the trivial and low level risks from the important environmental risks requires the application of sound scientific principles. Both the US EPA and the Washington Department of Ecology have examined the wealth of data and conducted risk assessments on triclopyr. They have both determined that triclopyr will have no significant acute or chronic impact on people, fish, or freshwater invertebrates when recommended rates are used.

#### 21. Is triclopyr one molecule away from Agent Orange?

The health effects of Agent Orange are linked to its dioxin contamination. Triclopyr does not contain toxic dioxin impurities so we do not need to be concerned about health effects of dioxins in the use of triclopyr.

The molecule of triclopyr acid is structurally similar to the two herbicides in Agent Orange.

- Agent Orange was an herbicide used extensively in the Vietnam war to defoliate large tracts of forest.
- Agent Orange contained two active ingredients: 2,4-D and 2,4,5-T. Triclopyr acid is one atom different from 2,4,5-T and two atoms different from 2,4-D.
- Triclopyr acid differs in an important feature. Triclopyr is based on a pyridine ring and 2,4,5-T is based on a phenol ring.

- This ring difference prevents dioxin impurities from forming during production of triclopyr.
- The principle health issue with Agent Orange was contamination with a highly toxic dioxin impurity (2,3,7,8- TCDD) formed during the synthesis of 2,4,5-T.
- Health effects observed in Airforce mixers, loaders, and sprayers; who experienced heavy occupational exposure to Agent Orange; have generally been ascribed to dioxin exposure.
- 2,4,5-T is now banned, largely because of unavoidable dioxin impurities formed during its production.
- Dioxin impurities do not occur in the synthesis of triclopyr because of the difference in the ring structure.
- There is no natural pathway for triclopyr to chemically convert to 2,4,5-T or form dioxins in the environment.

## 22. How many of the triclopyr studies have been funded - in whole or in part - by Dow Chemical or one of its subsidiaries? What is the level of potential conflict of interest here?

Most of the studies required by EPA for the registration for triclopyr as an aquatic herbicide have been funded by its manufacturer. This is normal since companies typically spend 20-50 million dollars in testing to meet EPA registration requirements for aquatic herbicides. EPA has extremely rigorous testing standards called Good Laboratory Practices that the laboratories must comply with. This helps ensure quality results. Who else, besides the company selling the product would be willing to invest this sort of money in toxicity testing? However, government agencies and Universities often conduct their own field trials and other research and these published results are considered by the state when conducting risk assessments. For instance the University of Washington has published studies on using triclopyr to control purple loosestrife. The Washington Department of Ecology and the University of Washington are conducting research on the impacts of triclopyr (and other aquatic herbicides) on the smoltification of juvenile coho and chinook salmon.

#### 23. What does "half-life" mean and what is the "half-life" of triclopyr?

Half life is the period of time that must elapse for a pesticide to breakdown to ½ its original concentration. The half-life varies dependent upon where the triclopyr is found (i.e. water, hydrosoil, etc.) and other environmental factors. Half-lives for triclopyr and its breakdown products average six days or less in water and 8.4 days or less in sediment. (Citation: Letter to Kathleen Emmett, Dept. of Ecology, March 18, 2004: Comments on Environmental Impact Statement for Permitted Use of Triclopyr – Draft from Brian L. Bret, Ph.D.). Renovate 3<sup>TM</sup> has been shown to drop to non-detectable levels in 24 hours – 15 days (typically 3-7) based upon immunoassay testing completed during the 2003 field season.

# 24. What does triclopyr "break down" into – are these elements harmful in any manner?

Triclopyr's eventual, final metabolite is carbon dioxide ( $CO_2$ ). To get there, it typically breaks down into trichloropyridinol or TCP, a compound that itself is far less stable than triclopyr in aquatic systems, as seen in aquatic field studies. TCP itself has a comparable level of toxicity as triclopyr and is frequently found at low concentrations in early sampling points in field studies. The methoxypyridine or TMP metabolite is rarely observed but also has a comparable level of toxicity as triclopyr and TCP.

#### 25. How long will the herbicide last in the lake water?

In natural water, sunlight and microorganisms rapidly degrade triclopyr. Triclopyr concentrations decline sharply over the first several days after treatment. Residues should be more than 95% degraded and dissipated from treated water in 1-2 weeks following treatment with triclopyr.

#### 26. Will triclopyr, be found in the sediment of lakes after treatment?

Renovate3<sup>TM</sup> degraded in the sediment in a relatively short period of time

### 27. What are the impacts that triclopyr could have on ground water?

The limited mobility of triclopyr in soil, low absorption constant, and high rate of microbial and photolytic degradation in water and sediment would indicate that this compound would have little potential for the extensive mobility required to contaminate groundwater supplies. This assumption is supported by data collected by the US Geological Survey (USGS), as this federal agency has collected over 850 groundwater samples over a five-year period in the Pacific Northwest area and these samples have been examined for pesticide residues. Triclopyr has never been detected in any of the groundwater samples taken by the USGS, despite extensive use as an herbicide in this region in forestry applications over a 20-year timeframe.

# 28. What will be the positive impacts of utilizing triclopyr to control Eurasian watermilfoil?

Triclopyr (Renovate 3<sup>TM</sup>) is selective to broad-leaved submersed aquatic plants such as Eurasian watermilfoil. Many native aquatic plants are not broad-leaved and are not significantly impacted by triclopyr. Significant reduction of Eurasian watermilfoil is a key component of improving and restoring the native aquatic plant community. If native species have less Eurasian watermilfoil to compete with they recover. There are additional benefits to the organisms that utilize these native species for food or shelter with the reduction of the Eurasian watermilfoil.

# 29. What are the risks associated with a "Do Nothing Alternative" in lakes with Eurasian watermilfoil?

Eurasian watermilfoil generally dominates the ecosystem to depths up to 20 feet (depending on the light conditions) and out-competes native submersed aquatic vegetation. The diversity of the aquatic vegetation community generally declines in Eurasian watermilfoil infested water bodies and this impacts the entire community within the lake. A plant such as Eurasian watermilfoil invades takes over and becomes a *keystone* species in a foreign environment/ecosystem. This changes and has negative impacts on the entire ecosystem.

#### 30. How can triclopyr kill only the milfoil and not other plants?

Broad-leaf plants (dicots) have different biochemistry than monocots. Triclopyr affects the family of broad-leafed plants or dicots. Eurasian watermilfoil is a broad-leaf plant whereas most native aquatic plants are monocots and not susceptible to triclopyr.

### 31. Is triclopyr a long term solution - or a short term fix?

Eurasian watermilfoil is extremely difficult to eradiate. If diver hand pulling of Eurasian watermilfoil can be successfully accomplished in the water body after the triclopyr treatment to remove remaining milfoil, then the triclopyr treatment could offer some long-term results.

# **32.** How will the die off of Eurasian watermilfoil plants in lakes after triclopyr treatment impact the lake?

Eurasian watermilfoil plants will slowly exhibit symptoms of herbicide damage (twisting of the stems due to the plant hormone (auxin-like) effect of triclopyr). The plants will gradually sink to the lake bottom and decompose. Systemic herbicides generally take a week to several weeks to entirely kill the plants so that you don't tend to get severe oxygen depletion that can sometimes occur when using contact herbicides. Native plants will fill in the areas left unoccupied by Eurasian watermilfoil.

## 33. Are there any species "at risk" with the use of triclopyr?

Broad-leaf aquatic plants, such as Eurasian watermilfoil, will be affected by triclopyr.

# 34. Where else has triclopyr been used? Were any problems encountered with these applications – to the environment, fish, wildlife etc.?

Renovate 3<sup>TM</sup> was labeled for use by the EPA in November of 2002. Prior to this triclopyr it had been used under an Experimental Use Permit as an aquatic herbicide since 1988 (for small test plots around the country). Additional field trials have been completed by researchers since 1984). A number of scientific papers by independent researchers have been published about field studies including studies in the Pend Oreille

River, Washington, and Lake Minnetonka Minnesota. Triclopyr has also been used for purple loosestrife control in Washington. In 2003 (Renovate 3<sup>TM</sup>'s first field season after EPA registration) it was used in 27 states on hundreds of projects. There have not been any reported problems encountered with these applications.

# 35. Is it true that some native plants take over a year to recover from an application of triclopyr?

Triclopyr is a selective herbicide which means that it generally targets the broad-leaved aquatic plants. Although there are few aquatic broad-leaved plants, there are others beside Eurasian watermilfoil. These species could be expected to be impacted by triclopyr. Eurasian watermilfoil is not thought to have viable seeds or other reproductive structures (besides fragments), whereas native aquatic plants have seeds, and sometimes tubers and other over-wintering structures. Even if the mature native plants are impacted by triclopyr, these plants should recover from their seeds or tubers the next season. Triclopyr treatment should enhance native plant growth since Eurasian watermilfoil crowds out native species. Removing Eurasian watermilfoil opens up niches that native species will fill. A study done in the the Pend Oreille River by the US Army Corps of Engineers with triclopyr documented that removing Eurasian watermilfoil markedly enhanced native plant growth in the treated areas.

### 36. Can milfoil plants develop immunity to triclopyr?

Short-term and long-term data collected by the U.S. Corps of Engineers Aquatic Plant Control Research Program (Vicksburg, MS) has not demonstrated that Eurasian watermilfoil is capable of developing immunity or "resistance" to triclopyr's mode of action. Work conducted by Dr. Kurt Getsinger and others with the Corps of Engineers indicates that "control of this species is likely" with appropriate dose regimes of triclopyr, which generally range from 0.5 to 2.5 ppm. The Corps of Engineers is particularly interested in the use of triclopyr to control milfoil for maintenance of waterways, as "this herbicide shows a low order of toxicity to microbial communities and higher aquatic organisms and residue accumulation in sediment, shellfish, and fish is negligible\*".

\*Netherland, M. and Getsinger, K. 1992. Efficacy of triclopyr on Eurasian watermilfoil: Concentration and exposure time effects. J. Aquatic Plant Management 30: 1-5.