

Appendix M

Delfin LNG Noxious Plant Control Plan

Onshore Facilities

for the

Port Delfin LNG Project

NOXIOUS PLANT CONTROL PLAN

May 2015

Submitted by:



Delfin LNG, LLC

1100 Louisiana Street, Suite 3550
Houston, TX 77002
(713) 714-2278

Prepared by:



TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1 INTRODUCTION	2
2 CHINESE TALLOW TREE	4
2.1 Status and Background Information	4
2.1.1 Summary	4
2.1.2 Characteristics	5
2.1.3 Life History	5
2.1.4 Origin and Distribution	5
2.1.5 Similar Species	6
2.1.6 Habitat	6
2.2 Control Plan	6
2.2.1 Control Field Personnel Qualifications	6
2.2.2 Mechanical Control	6
2.2.3 Herbicidal Control	6
2.2.4 Chinese Tallow Sapling Control	7
2.2.5 Chinese Tallow Control Frequency	7
3 REFERENCES	8

ACRONYMS AND ABBREVIATIONS

Port Delfin LNG Project	Delfin LNG, LLC's liquefied natural gas project, including all onshore and offshore components
Delfin LNG	Delfin LNG, LLC; <i>also</i> the Applicant
Port Delfin	the offshore component of the Port Delfin LNG Project consisting of the floating liquefied natural gas vessels, foundations, and underwater elements
DOF	Delfin onshore facilities; the onshore component of the Port Delfin LNG Project, consisting of an onshore pipeline, a compressor station, a supply header, and a meter station, located in Cameron Parish, Louisiana
DWP	deepwater port
DWPA	Deepwater Port Act of 1974, as amended
FERC	Federal Energy Regulatory Commission; <i>also</i> the Commission
FLNGV	floating liquefied natural gas vessel
FTA	Free Trade Agreement
HIOS	High Island offshore system
hp	horsepower
kW	kilowatt
LNG	liquefied natural gas
MARAD	Maritime Administration
NGA	Natural Gas Act
OCA	Outer Continental Shelf
SE-EPPC	Southeast Exotic Pest Plant Council
UTOS	U-T offshore system
USCG	U.S. Coast Guard

1 INTRODUCTION

Delfin LNG LLC (Delfin LNG; *also* the Applicant), a Louisiana limited liability company, is proposing to develop a deepwater port (DWP) terminal (referred to herein as Port Delfin) and associated offshore pipeline (collectively, the DWP) in the Gulf of Mexico to serve the liquefied natural gas (LNG) export market, all as more fully described in Delfin's application for authorization from the Secretary of Transportation, as delegated to the Maritime Administration (MARAD) and the United States Coast Guard (USCG), pursuant to the Deepwater Port Act of 1974, as amended (DWPA). The Delfin onshore facilities (DOF) and DWP are referred to collectively as the Project (Project).

In connection with the Project, Delfin is seeking authorization from the Federal Energy Regulatory Commission (FERC) (*or* the Commission) under Section 7(c) of the NGA to site, construct, and operate the DOF, which includes onshore pipelines and associated metering and compression facilities, the primary purpose of which is to measure and deliver gas into the offshore pipeline for the DWP. The DOF comprises the following facilities on the landward side of the mean, high water mark in Cameron Parish, Louisiana:

Onshore UTOS Pipeline. The UTOS pipeline is an existing approximately 1.1 mile section of the onshore portion of the former UT offshore system (UTOS)¹ pipeline, located landward of the high water mark to Transcontinental Gas Pipe Line, LLC (Transco) Station 44, that will be reactivated. Other existing appurtenant facilities associated with the former UTOS pipeline include a mainline block valve and blowdown site located south of Louisiana Highway 82.

Meter Station. Delfin proposes to install a new meter station located on the Transco Station 44 property that will meter and regulate pipeline-quality gas, to be supplied by interconnections with existing natural gas pipelines at Transco Station 44, which include the ANR Pipeline Company, the Natural Gas Pipeline Company of America, the Tennessee Gas Pipeline, and Transco. The meter station and interconnecting piping will be located entirely within the fence of the existing Transco Station 44 property. The meter station would meter all supply gas entering the facility from the supply gas header.

Supply Header. A new supply header would connect the meter station at Transco Station 44 and the new compression site, consisting of 0.25 mile of new 42-inch pipeline to connect the former UTOS pipeline to the new metering facilities and 0.6 mile of new 30-inch twin pipelines.

Compressor Station. The compressor station would consist of the following equipment or facilities:

- Four 32,000 horsepower ISO-rated (hp) Solar Titan 250 gas turbine-driven compressors
- Three 600 kilowatt (kW) Waukesha VHP 3604 generators with Waukesha F3524GSI engines
- Two control buildings
- Office and warehouse buildings
- Pig launcher

¹ As set forth more fully in the Application, the UTOS pipeline system was formally abandoned by its prior owner, Enbridge, and no longer exists as a legal entity. The naming convention is retained for ease of reference but technically describes the "former UTOS" pipeline system that is now owned by Delfin Offshore Pipeline LLC, a wholly owned subsidiary of Delfin LNG LLC, "the Applicant."

Port Delfin LNG Project

- Check meter.

The location of the facilities is more fully set forth in Exhibit F to the Application. Section 1.3, RR 1, describes the DOF in greater detail. Figure 1.2-2 in RR 1 provides an aerial overview of the DOF.

The entirety of the DOF facilities and associated temporary construction activities would be located within the boundaries of existing rights-of-way (ROWs) on land already devoted to energy infrastructure use. Specifically, the meter station and interconnecting piping will be located within an approximately 200-foot by 150-foot fenced, graveled area on Transco's Station 44. The two new 30-inch supply header pipelines and associated pipeline ROW will stay within the boundaries of the PSI Midstream Partners, L.P. Cameron Meadows Gas Plant (PSI), on property to be owned by Delfin LNG, and the adjacent Transco Station 44 property, all in Cameron Parish, Louisiana. Delfin LNG has executed a letter of intent with PSI to purchase the property on which the compressor station would be located and anticipates entering into an easement agreement for the supply header on PSI-owned property. Delfin LNG currently owns lease rights to construct and operate facilities at Transco Station 44.

The Project's offshore pipeline (which is not subject to Commission jurisdiction but is described here to provide context) includes the portion of the former UTOS pipeline beginning at the seaward side of the mean high water mark, connecting via a 700-foot bypass to the High Island Offshore System, LLC (HIOS) pipeline at West Cameron Block 167, and extending via the HIOS pipeline to the proposed Port Delfin and beyond (terminating at High Island Block A264). No separate facilities delineate the point of jurisdictional distinction between the on-shore pipeline subject to the Commission's jurisdiction and the remainder of the former UTOS pipeline that continues offshore and that will be part of the DWP.

The Project would provide a new use for existing gas pipelines that were historically used to transport offshore natural gas production to shore. Feed gas would be transported through the former UTOS pipeline now owned by Delfin LNG. At the terminus of that pipeline, the gas would bypass the existing manifold platform located at WC 167 approximately 28.4 miles offshore in the Gulf of Mexico and continue on to the existing 42-inch-diameter HIOS pipeline. The new WC 167 bypass would be a sub-sea 42-inch diameter pipeline approximately 700-feet long directly connecting the former UTOS to HIOS. The UTOS portion of this pipeline system is currently idled, isolated, and preserved (in a manner such that it can be fully returned to active service), and was placed in this mode in accordance with all applicable regulations due to declining offshore production in the general area. The presently operating HIOS system is underutilized for similar reasons and HIOS, LLC (which is owned by Genesis Energy LP²) and Delfin LNG have entered into a Pipeline Services Agreement providing Delfin LNG the exclusive right to utilize the HIOS pipeline from WC 167 to HI A264 as part of its Project (with no other shippers). HIOS is filing an application, contemporaneously with this Amended Application, with the FERC to abandon its FERC-jurisdictional services over the pipeline to allow for this new use of its pipeline as part of the Project.

The primary purpose of the Project is to provide a safe and reliable facility to liquefy natural gas that Delfin LNG's customers will export to free trade agreement (FTA) and non-FTA nations. Port Delfin would consist of four moored, floating, LNG vessels (FLNGVs) capable of receiving the pipeline-quality feed gas from the offshore pipeline, cooling it to produce LNG, storing the LNG within internal tanks onboard each of the FLNGVs, and loading the LNG onto trading carriers through ship-to-ship transfer for export. The purpose of the DOF is to receive gas from the interstate pipeline grid and deliver it into the DWP.

² Genesis Energy LP recently acquired Enterprise Products Partners' offshore pipelines and services in the Gulf of Mexico. Genesis operations include inshore and offshore pipeline transportation, marine transportation, and supply and logistics.

2 CHINESE TALLOW TREE

Under Louisiana Revised Statute 3:1791, one noxious plant is listed, the Chinese tallow tree (*Sapium sebiferum*). The presence of the Chinese tallow tree was noted throughout the proposed forested areas of the DOF during field surveys conducted in December 2014 and January 2015. Active control of this species is required to prevent it from dominating the areas that will be disturbed during construction. The noxious plant control measures in this plan will be implemented and procedures will be coordinated with concurrence of the landowners.

Due to the presence of the Chinese tallow tree at the DOF, there is concern that this invasive species will establish and spread along portions of the construction footprint, including the construction areas during site restoration and revegetation. This document presents the control plans that Delfin LNG has developed to prevent establishment and spread of the Chinese tallow tree in areas that will be disturbed during construction activities.

The following sections provide detailed information about the Chinese tallow tree, including identification, growth cycle, and control methods that will be implemented by year.

2.1 Status and Background Information

The Chinese tallow tree is an aggressive woody invader of wetland, coastal, and disturbed habitats and has been shown to reduce native species diversity and richness and alter ecosystem structure and functionality in natural areas. The Chinese tallow tree was introduced into the United States from Japan and China, first as a seed oil crop in the late eighteenth century and then later as an ornamental.

The Chinese tallow tree is an early successional tree with life history traits that enable it to thrive in unstable or unpredictable environments; these traits include high fecundity, relatively small size, short generation time, and the ability to disperse propagules widely. It is a superior competitor in its new range, has virtually no specialist herbivore or pathogen loads, can readily occupy “vacant niches,” and can alter ecosystem processes such as nutrient cycling and stand structure. In Louisiana, the Chinese tallow tree has been shown to convert herbaceous coastal prairies into closed canopy tallow forests within a decade of establishment, if not controlled (Bruce et al. 1995). The species description and control information provided below was adapted from the Southeast Exotic Pest Plant Council (SE-EPPC) guidelines (2008).

2.1.1 Summary

The Chinese tallow tree is a small to medium-sized deciduous tree in the Euphorbiaceae (Spurge) family. It is monoecious, producing male and female flowers on the same plant. As with many species in the Euphorbia family, the tallow tree is toxic to animals and humans. The white sap may be a skin irritant. It is native to China and Japan where the waxy outer covering of the seed is used for machine oil, soap making, fuel oil, and many other uses.

The Chinese tallow tree represents a significant invasive species problem in many areas of Louisiana and across the southern United States. It adversely affects the diversity of native plants by invading and eventually dominating habitats ranging from marshes, to coastal prairies, to river bottoms, to upland forests, as well as disturbed sites and abandoned agricultural fields. The tree prefers wet soils but is very adaptable.

Port Delfin LNG Project

The Chinese tallow tree can turn areas into a single-species forest. It has been widely planted as an ornamental tree in many parts of Louisiana, but this practice is discouraged. The rapid forestation of the Chinese tallow tree has contributed significantly to the degradation of wetlands along the Gulf Coast. It is believed that the tree may alter soil chemistry, allowing the species to self-perpetuate once established.

Insects, diseases, and other natural enemies have little if any impact on Chinese tallow tree. Cattle and horses will not graze on it. Although it is subject to freeze damage, freezes rarely kill the roots. Cold temperatures, however, will prevent this tree from becoming a significant problem in northern portions of its range in the United States.

Research is being conducted to find ways to effectively control Chinese tallow trees without causing environmental harm. Fire can successfully eliminate small trees, but large trees tend to re-sprout in burn areas and fire may exacerbate infestations (McCormick 2005). Knocking down the trees with grading equipment is not effective if roots remain to allow prolific sprouting. The entire tree system should be removed when possible. Debris should be segregated for off-site disposal. Herbicides will provide temporary control, but repeated applications are necessary.

2.1.2 Characteristics

Height. Chinese tallow tree can reach a height of 15 meters at maturity.

Leaves. The leaves are rhombic ovate, 4 to 7 centimeters long and 3.5 to 6 centimeters wide. The tip of the leaf is acuminate (pointed) with a rounded to truncate (flattened) base. The leaf surface is glabrous with smooth margins and prominent venation. The leaf stalks are 2 to 5 centimeters long with two prominent glands just below the leaf. Leaves are placed alternately on the stem.

Flowers. The terminal flowers are in greenish-yellow spike-like bundles. The staminate (male) flowers occur in fascicles of 3 to 15 on the upper portion of the flower. The solitary pistillate (female) flowers are on pedicels at the base of the spike.

Fruit. The 1- to 1.3-centimeter capsule has three locules (compartments) turning from green to black upon maturity. The capsule walls are eventually shed, exposing the seeds.

Seeds. The three seeds per capsule are round, white, and 7 to 8 millimeters in size.

2.1.3 Life History

Growth initiates in early spring and flowers are produced from March through May. Flowering can begin when the trees are 1 meter tall, which may be as early as three years of age, depending on growing conditions. The male and female seed clusters mature at different times. Variation is seen between sub-populations as to which type matures first. This contributes to the high genetic diversity of this species. The seeds mature in late summer to fall. Seeds are produced annually and each tree has the potential of bearing 100,000 seeds. Trees remain productive throughout their lives, which is commonly up to 25 years, although trees of 100 years of age have been recorded. Seeds are distributed primarily via birds and water. Trees readily re-sprout from stumps and rootstocks.

2.1.4 Origin and Distribution

The Chinese tallow tree was introduced into the United States in the 1700s in South Carolina. It was distributed in the Gulf Coast in the 1900s by the U.S. Department of Agriculture in an attempt

Port Delfin LNG Project

to establish a soap-making industry. Current distribution includes all of the Southeastern United States from Texas to Florida and from North Carolina to Arkansas, and it was recently discovered in California.

2.1.5 Similar Species

The Chinese tallow tree resembles several species of poplar (*Populus* sp.) trees. The main distinguishing feature is that the tallow tree has smooth margins on the leaves while poplar leaves are serrated.

2.1.6 Habitat

Tallow tree prefers mesic to hydric soils, but it can tolerate a wide range of soil conditions. It is commonly found in bottomlands, old fields, coastal prairies, and riparian areas. It can become established in shaded areas and is capable of spreading into undisturbed as well as disturbed areas; it is tolerant of periodic flooding and exposure to saltwater.

2.2 Control Plan

2.2.1 Control Field Personnel Qualifications

The Chinese tallow tree control plan requires mechanical (cutting and hand pulling) and potentially chemical treatment to effectively remove this species during site preparation. Chinese tallow tree control field personnel will be trained to identify Chinese tallow tree and use the prescribed mechanical and chemical treatment procedures. Additionally, these individuals will have the applicable training and registration to purchase, handle, and apply regulated herbicides used for Chinese tallow tree control.

An accompanying health and safety plan will be developed and implemented in conjunction with this control plan. The control methods specified in this plan will be implemented as appropriate. Control of Chinese tallow tree within the permitted construction workspace will be in accordance with landowner agreements.

2.2.2 Mechanical Control

Grading and topsoil segregation construction techniques typically leave Chinese tallow trees systems behind, which allows for prolific re-sprouting. The entire tree system should be removed when possible. Vegetative debris containing Chinese tallow tree or its seeds should be segregated from other plant material for off-site disposal. Rootstock should be ground if on-site disposal is required.

Field personnel will cut any remaining Chinese tallow trees found within the workspaces at ground level with power equipment or manual saws (SE-EPPC 2008). Debris will be gathered and transported to an approved off-site disposal facility.

Cutting is most effective when trees have begun to flower to prevent seed production. Because Chinese tallow tree spreads by suckering, re-sprouts are common after treatment. Cutting is an initial control measure and will require either an herbicidal control or repeated cutting of re-sprouts.

2.2.3 Herbicidal Control

Reports indicate that spring herbicide application may not be successful, and late summer to early fall herbicide applications should be employed to translocate (i.e., transport the herbicide into the root

Port Delfin LNG Project

system by natural circulation within the plant) the herbicide into the plant most effectively (The Nature Conservancy 2011).

Herbicide applications should be used when the species has been cut and removed but the stump is left in place. Stump treatments can be used as long as the ground is not frozen. It is common practice to use diesel or other oil as an application medium for several herbicides; however, Delfin LNG will not use diesel for herbicide applications. This stump treatment method would likely be utilized in wetland areas where it is desirable to leave woody plant root systems in place for soil stabilization during construction. Herbicides used and treatment method are as follows:

Glyphosate: Horizontally cut stems at or near ground level. Immediately apply a 50 percent solution of glyphosate and water to the cut stump, covering the outer 20 percent of the stump (SE-EPPC 2008). Since glyphosate is non-selective, it is very important to protect the surrounding desirable plants. Thus, a sponge or similar discrete application method will be used to apply the glyphosate solution. The water mixed with glyphosate must be free of dirt because this herbicide binds tightly to soil clay and organic matter and the effectiveness of the application would be reduced.

Triclopyr: Horizontally cut stems at or near ground level. Immediately apply a 50 percent solution of triclopyr and water to the cut stump, covering the outer 20 percent of the stump (SE-EPPC 2008). In areas where desirable grasses are growing under and around Chinese tallow, the SE-EPPC (2008) reports that triclopyr can be used without non-target damage.

2.2.4 Chinese Tallow Sapling Control

Chinese tallow is effectively controlled by removal of young seedlings; hand- or machine-pulling of seedlings and saplings provides excellent control. Plants should be pulled as soon as they are large enough to grasp but before they produce seeds. Seedlings are best pulled after a rain when the soil is loose. The entire root must be removed since broken fragments may re-sprout (SE-EPPC 2008).

2.2.5 Chinese Tallow Control Frequency

Because Chinese tallow is a successful invasive species, there is always a potential for the plant to establish. However, the goal of this plan is to allow native and other desirable plants sufficient opportunity to establish within areas disturbed during construction.

Prior to construction. A pre-construction survey within the construction footprint was conducted. Chinese tallow trees were noted throughout the site.

During construction. Delfin LNG will conduct cutting and on-site burning or off-site disposal of debris during construction preparation activities.

During construction demobilization. Delfin LNG will apply chemical (herbicide) treatment as described above during construction demobilization. Delfin LNG will record treatment locations and herbicide(s) volumes used during this effort.

Post-construction - Late-summer. Delfin LNG will apply a final chemical (herbicide) treatment to stumps and roots exhibiting sprouts. In addition, saplings will be removed by pulling as described above. Delfin LNG will record treatment locations and herbicide(s) volumes used during this effort.

3 REFERENCES

- Bruce, K.A., G.N. Cameron, P.A. Harcombe, and G. Jubinsky. 1997. Introduction, impact on native habitats, and management of a woody invader, the Chinese tallow tree, *Sapium sebiferum* (L.) Roxb. *Natural Areas Journal* 17:255-260.
- McCormick, C. 2005. Chinese Tallow Management Plan for Florida: A Report from The Florida Exotic Pest Plant Council's Chinese Tallow Task Force. Accessed December 11, 2014: http://www.fleppc.org/Manage_Plans/Tallow_Plan.pdf.
- Southeast Exotic Pest Plant Council (SE-EPPC). 2008. Southeast Exotic Pest Plant Council Invasive Plant Manual. Chinese Tallowtree. Accessed December 11, 2014. <http://www.se-eppc.org/manual/SASE.html>.
- The Nature Conservancy. 2011. Element Stewardship Abstract for *Sapium sebiferum* – Chinese tallow-tree, Florida aspen, popcorn tree. Accessed December 11, 2014. <http://www.invasive.org/weedcd/pdfs/tncweeds/sapiseb.pdf>.
- Tu, M., C. Hurd, and J.M. Randall. 2001. Weed Control Methods Handbook: Tools and Techniques for Use in Natural Areas. The Nature Conservancy Wildland Invasive Species Team, April 2001. Accessed December 11, 2014: <http://invasive.org/gist/products/handbook/methods-handbook.pdf>.

Appendix A Herbicide Information Sheets

Glycosphate and Triclopyr
(Source: Tu, Hurd, and Randall 2001)

Herbicide Details

Chemical Formula: N-(phosphonomethyl) glycine

Trade Names: Monsanto discovered and held the patent for glyphosate, and was for many years, the only company that manufactured and sold this herbicide. The patent expired in 2000, however, and already several other companies are making and selling glyphosate formulations. Some of the current trade names include: Roundup Ultra[®], Roundup Pro[®], Accord[®], Honcho[®], Pondmaster[®], Protocol[®], Rascal[®], Expedite[®], Ranger[®], Bronco[®], Campaign[®], Landmaster[®], and Fallow Master[®] by Monsanto; Glyphomax[®] and Glypro[®] by Dow AgroSciences; Glyphosate herbicide by Du Pont; Silhouette[®] by Cenex/Land O'Lakes; Rattler[®] by Helena; MirageR[®] by Platte; JuryR[®] by Riverside/Terra; and Touchdown[®] by Zeneca. As of November 2001, Rodeo[®] (previously manufactured by Monsanto) is now being manufactured by Dow AgroSciences and Monsanto is now producing Aquamaster[®].

Manufacturers: Current manufacturers include Monsanto, Cenex/Land O'Lakes, Helena, Platte, Riverside/Terra, Dow AgroSciences, and Zeneca.

Use Against Natural Area Weeds: Glyphosate is a broad-spectrum, nonselective systemic herbicide that kills or suppresses many grasses, forbs, vines, shrubs, and trees. Care should be taken, especially in natural areas, to prevent it from being applied to desirable, native plants, because it will likely kill them. In terrestrial systems, glyphosate can be applied to foliage, green stems, and cut-stems (cut-stumps), but cannot penetrate woody bark (Carlisle & Trevors 1988). Only certain formulations of glyphosate (e.g., Rodeo[®]) are registered for aquatic use, as glyphosate by itself is essentially non-toxic to submersed plants (Forney & Davis 1981), but the adjuvants often sold with glyphosate may be toxic to aquatic plants and animals.

Glyphosate is one of the most commonly used herbicides in natural areas, because it provides effective control of many species. Natural area weeds that have been controlled with glyphosate include: bush honeysuckle (*Lonicera maackii*), cogon grass (*Imperata cylindrica*), common buckthorn (*Rhamnus cathartica*), glossy buckthorn (*Frangula alnus*), Japanese honeysuckle (*Lonicera japonica*), and smooth brome (*Bromus inermis*). In TNC preserves, glyphosate has been used to control dewberries (*Rubus* spp.), bigtooth aspen (*Populus grandidentata*), and black cherry (*Prunus serotina*) at Kitty Todd preserve in Ohio, sweetclover (*Melilotus officinalis*) in Indiana preserves, leafy spurge (*Euphorbia esula*) and St. John's wort/Klamath weed (*Hypericum perforatum*) in Michigan preserves, and bindweed (*Convolvulus arvensis*) and velvetgrass (*Holcus lanatus*) in Oregon and Washington preserves.

In aquatic or wetland systems, glyphosate has successfully controlled common reed (*Phragmites australis*) in Delaware, Michigan, and Massachusetts preserves, purple loosestrife (*Lythrum salicaria*) in Indiana and Michigan preserves, reed canarygrass (*Phalaris arundinacea*) in Illinois preserves, and glossy buckthorn (*Frangula alnus*) and hybrid cattail (*Typha x glauca*) in Michigan preserves.

Mode of Action: Glyphosate kills plants by inhibiting the activity of the enzyme 5-enolpyruvylshikimic acid-3-phosphate synthase (EPSP), which is necessary for the formation of the aromatic amino acids tyrosine, tryptophan, and phenylalanine. These amino acids are important in the synthesis of proteins that link primary and secondary metabolism (Carlisle & Trevors 1988). EPSPs are present in the chloroplast of most plant species, but are not present in animals. Animals need these three amino acids, but obtain them by eating plants or other animals.

Glyphosate is therefore, relatively non-toxic to animals (Monsanto Company 1985). Certain surfactants or other ingredients that are added to some glyphosate formulations are toxic to fish and other aquatic species (EXTOXNET 1996).

Glyphosate can also act as a competitive inhibitor of phosphoenolpyruvate (PEP), which is one of the precursors to aromatic amino acid synthesis. It also affects other biochemical processes, and, although these effects are considered secondary, they may be important in the total lethal action of glyphosate.

Dissipation Mechanisms:

Summary: Glyphosate is degraded primarily by microbial metabolism. Glyphosate is believed to be susceptible to photodegradation (Lund-Hoie & Friestad 1986), but the extent to which this occurs is uncertain. Glyphosate is not significantly degraded by other chemical mechanisms in the field. Glyphosate is strongly adsorbed to soil, which can slow microbial metabolism but prevents excessive movement in the environment. Glyphosate is non-volatile (T. Lanini, pers. obs).

Volatilization

Glyphosate does not volatilize readily when applied in the field (T. Lanini, pers. obs.).

Photodegradation

Although originally thought to be unaffected by sunlight (Rueppel et al. 1977), later studies found glyphosate to be susceptible to photodegradation (Lund-Hoie & Friestad 1986; Carlisle & Trevors 1988). Lund-Hoie and Friestad (1986) reported a half-life of four days for glyphosate in deionized water under UV light.

Microbial Degradation

Glyphosate is degraded primarily by microbial metabolism. Two steady rates of degradation have been identified (Rueppel et al. 1977). It has been hypothesized that the more rapid rate of degradation represents the metabolism of unbound glyphosate molecules, while the slower rate represents the metabolism of glyphosate molecules bound to soil particles (Nomura & Hilton 1977; Rueppel et al. 1977). The degradation of glyphosate is slower in soils with a higher adsorption capacity. Degradation rate was also affected by the particular microbial community of each soil (Carlisle & Trevors 1988; Malik et al. 1989). The primary metabolite of glyphosate is aminomethylphosphonic acid, which is non-toxic and degraded microbially at a somewhat slower rate than the parent compound (Nomura & Hilton 1977; Rueppel et al. 1977;

Carlisle & Trevors 1988). A number of other minor, biodegradable metabolites have also been identified.

Adsorption

Glyphosate is water-soluble, but it has an extremely high ability to bind to soil particles. Adsorption of glyphosate increases with increasing clay content, cation exchange capacity, and decreasing soil pH and phosphorous content (Sprankle et al. 1975a,b; Hance 1976; Nomura & Hilton 1977; Rueppel et al. 1977; Glass 1987). Glyphosate is adsorbed to soil particles rapidly during the first hour following application and slowly thereafter (Sprankle et al. 1975b). Strong adsorption to soil particles slows microbial degradation, allowing glyphosate to persist in soils and aquatic environments. Because glyphosate rapidly binds to soils, it has little or no herbicidal activity (“killing power”) once it touches soil (Sprankle et al. 1975a; Hance 1976; Nomura & Hilton 1977). Glyphosate can also be inactivated by adsorption if mixed with muddy water.

Adsorption prevents glyphosate from being mobile in the environment except when the soil particles themselves are washed away (Sprankle et al. 1975b; Rueppel et al. 1977; Roy et al. 1989a). Comes et al. (1976) found that glyphosate sprayed directly into a dry irrigation canal was not detectable in the first irrigation waters flowing through the canal several months later, although glyphosate residues remained in the canal soils. In most cases, glyphosate is quickly adsorbed to suspended and bottom sediments (Feng et al. 1990).

Chemical Decomposition

Glyphosate is not readily hydrolyzed or oxidized in the field (Rueppel et al. 1977; Anton et al. 1993; Zaranyika & Nyandoro 1993).

Behavior in the Environment

Summary: Glyphosate binds readily with soil particles, which limits its movement in the environment. It is degraded through microbial metabolism with an average half-life of two months in soils and two to ten weeks in water. In plants, glyphosate is slowly metabolized.

Soils

Glyphosate is highly water soluble, but unlike most water-soluble herbicides, glyphosate has a very high adsorption capacity. Once glyphosate contacts soil it is rapidly bound to soil particles rendering it essentially immobile (Roy et al. 1989a; Feng & Thompson 1990). Unbound glyphosate molecules are degraded at a steady and relatively rapid rate by soil microbes (Nomura & Hilton 1977; Rueppel et al. 1977). Bound glyphosate molecules also are biologically degraded at a steady, but slower rate. The half-life of glyphosate in soil averages two months but can range from weeks to years (Nomura & Hilton 1977; Rueppel et al. 1977; Newton et al. 1984; Roy et al. 1989a; Feng & Thompson 1990; Anton et al. 1993). Although the strong adsorption of glyphosate allows residues to persist for over a year, these residues are largely immobile and do not leach significantly. Feng and Thompson (1990) found that >90% of glyphosate residues were present in the top 15 cm of soil and were present as low as 35 cm down the soil column in only one of 32 samples. Adsorption to soil particles prevents glyphosate from being taken-up by the roots of plants.

Glyphosate Water

7e.5

Because glyphosate binds strongly to soils, it is unlikely to enter waters through surface or sub-surface runoff except when the soil itself is washed away by runoff, and even then, it remains bound to soil particles and unavailable to plants (Rueppel et al. 1977, Malik et al. 1989). Most glyphosate found in waters likely results from runoff from vegetation surfaces, spray drift, and intentional or unintentional direct overspray. In most cases, glyphosate will dissipate rapidly from natural water bodies through adsorption to organic substances and inorganic clays, degradation, and dilution (Folmar et al. 1979; Feng et al. 1990; Zaranyika & Nyandoro 1993; Paveglio et al. 1996). Residues adsorbed to suspended particles are precipitated into bottom sediments where they can persist until degraded microbially with a half-life that ranges from 12 days to 10 weeks (Goldsborough & Brown 1993; EXTTOXNET 1996). At least one study found that >50% of the glyphosate added directly to the waters of an irrigation canal were still present 14.4 km downstream (Comes et al. 1976).

Vegetation

Glyphosate is metabolized by some, but not all plants (Carlisle & Trevors 1988). It is harmless to most plants once in the soil because it is quickly adsorbed to soil particles, and even when free, it is not readily absorbed by plant roots (Hance 1976). The half-life of glyphosate on foliage has been estimated at 10.4 to 26.6 days (Newton et al. 1984). Roy et al. (1989b) found 14% and 9% of applied glyphosate accumulated in the berries of treated blueberry and raspberry bushes, respectively. These residues dissipated from the fruit with a half-life of <20 days for blueberries and <13 days for raspberries (Roy et al. 1989b).

Environmental Toxicity

Birds and Mammals

Glyphosate is of relatively low toxicity to birds and mammals (Evans & Batty 1986). The LD50 of glyphosate for rats is 5,600 mg/kg and for bobwhite quail, >4,640 mg/kg. EPA's Re-registration Eligibility Decision states that blood and pancreatic effects and weight gain were noted during subchronic feeding studies with rats and mice (EPA 1993). Other studies show developmental and reproductive impacts to animals given the highest dose.

Newton et al. (1984) examined glyphosate residues in the viscera of herbivores following helicopter application of glyphosate to a forest in Oregon and found residue levels comparable to those found in litter and ground cover (<1.7 mg/kg). These residue levels declined over time and were undetectable after day 55 (Newton et al. 1984). Although carnivores and omnivores exhibited much higher viscera residue levels (5.08 mg/kg maximum), Newton et al. (1984) concluded that carnivores were at lower risk than herbivores due to the lower relative visceral weights and a proportionally lower level of food intake.

Batt et al. (1980) found no effect on chicken egg hatchability or time to hatch when an egg was submerged in a solution of 5% glyphosate. Sullivan and Sullivan (1979) found that black-tailed deer showed no aversion to treated foliage and consumption of contaminated forage did not reduce total food intake. Significant impacts to bird and mammal populations due to large-scale habitat alterations following treatment of forest clearcuts with glyphosate have been reported (Morrison & Meslow 1984; Santillo et al. 1989a,b; MacKinnon & Freedman 1993).

Aquatic Species

Glyphosate itself is of moderate toxicity to fish. The 96-hour LC50 of technical grade glyphosate for bluegill sunfish and rainbow trout are 120 mg/L and 86 mg/L, respectively. Fish exposed to 5 mg/L of glyphosate for two weeks were found to have gill damage and liver damage was observed at glyphosate concentrations of 10 mg/L (Neskovic et al. 1996). The technical grade of glyphosate is of moderate toxicity to aquatic species, and the toxicity of different glyphosate formulations can vary considerably. For example, Touchdown 4-LC[®] and Bronco[®] have low LC50s for aquatic species (<13 mg/L), and are not registered for aquatic use. On the other hand, Rodeo[®] has relatively high LC50s (>900 mg/L) for aquatic species and is permitted for use in aquatic systems. The surfactant in Roundup[®] formulations is toxic to fish, however, Rodeo[®] has no surfactant, and is registered for aquatic use.

The surfactant X-77 Spreader[®], which is often used in conjunction with Rodeo[®], is approximately 100 times more toxic to aquatic invertebrates than Rodeo[®] alone (Henry et al. 1994). The surfactant MONO818[®] is included in Roundup[®] formulations because it aids the break-down of surface tension on leaf surfaces, but it may also interfere with cutaneous respiration in frogs and gill respiration in tadpoles (Tyler 1997 a,b). In addition, MONO818[®] is highly toxic to fish (Folmar et al. 1979; Servizi et al. 1987). The LC50 of MONO818[®] is 2-3 mg/L for sockeye, rainbow, and coho fry (Folmar et al. 1979; Servizi et al. 1987; Tyler 1997 a,b). The LC50 of Roundup[®] for bluegill sunfish and rainbow trout is only slightly higher at 6-14 mg/L and 8-26 mg/L, respectively. Similarly for *Daphnia*, the 96-hour LC50 of glyphosate alone is 962 mg/L, but the LC50 of Roundup[®] drops to 25.5 mg/L (Servizi et al. 1987). Roundup[®] is therefore not registered for use in aquatic systems.

Despite these toxicity levels, Hildebrand et al. (1980) found that Roundup[®] treatments at concentrations up to 220 kg/ha did not significantly affect the survival of *Daphnia magna* or its food base of diatoms under laboratory conditions. In addition, Simenstad et al. (1996) found no significant differences between benthic communities of algae and invertebrates on untreated mudflats and mudflats treated with Rodeo[®] and X-77 Spreader[®]. It appears that under most conditions, rapid dissipation from aquatic environments of even the most toxic glyphosate formulations prevents build-up of herbicide concentrations that would be lethal to most aquatic species.

Other Non-Target Organisms

Roberts and Berk (1993) investigated the effects of Roundup[®] on chemoattraction of the protozoa *Tetrahymena pyriformis* and found that it significantly interfered with chemoreception but not motility. Doses of glyphosate <10 ppm were stimulatory to soil microflora including actinomycetes, bacteria, and fungi, while concentrations > 10 ppm had detrimental impacts on microflora populations in one study (Chakravarty & Sidhu 1987). While some short-term studies (< 30 days) found glyphosate caused significant impacts to microbial populations, Roslycky (1982) found that these populations rebound from any temporary increase or decrease within 214 days. Similarly, Tu (1994) found that microorganisms recovered rapidly from treatment with glyphosate and that the herbicide posed no long-term threat to microbial activities.

Application Considerations:

Glyphosate can be applied using conventional, recirculating, wet apron, hooded and hand-operated sprayers; controlled drop, rope-wick, roller, and carpet applicators; mistblowers; injectors; and wipe-on devices (Carlisle & Trevors 1988). Feng et al. (1990) found that 10 meter buffer zones limited unintentional effects through chemical drift and off-target deposits into streams during application, while Marrs et al. (1993) concluded that 20 meters was a safe buffer width. Liu et al. (1996) found that increasing the glyphosate concentration was more effective in controlling weeds than increasing the droplet size. Thielen et al. (1995) concluded that the cations of hard water, including Ca^{++} and Mg^{++} , can greatly reduce the efficacy of glyphosate when present in a spray solution. Addition of ammonium sulfate or other buffer can precipitate out heavy elements in “hard” water if added before the herbicide is mixed with water.

When glyphosate is used as an aquatic herbicide, do not treat the entire water body at one time. Treat only one-third to one-half of any water body at any one time, to prevent fish kills caused by dissolved oxygen depletion.

Safety Measures:

Some glyphosate formulations are in EPA toxicity categories I and II (the two highest categories) for eye and skin exposure. Care should be taken and protective clothing worn to prevent accidental contact of these formulations on skin or eyes.

Human Toxicology:

EPA classified glyphosate as a “Group E” carcinogen or a chemical that has not shown evidence of carcinogenicity in humans (EPA 1993).

References

- Anton, F.A., et al. 1993. Degradational behavior of the pesticides glyphosate and diflufenbuzon in water. *Bulletin of Environmental Contamination and Toxicology* 51:881-888.
- Batt, B.D., J.A. Black and W.F. Cowan. 1980. The effects of glyphosate herbicide on chicken egg hatchability. *Canadian Journal of Zoology* 58:1940-1942.
- Carlisle, S. M., and J. T. Trevors. 1988. Glyphosate in the environment. *Water Air Soil Pollution*. 39:409-420.
- Chakravarty, P., and S. S. Sidhu. 1987. Effect of glyphosate, hexazinone and triclopyr on in vitro growth of five species of ectomycorrhizal fungi. *Eur. J. For. Path.* 17:204-210.
- Comes, R.D., V.F. Bruns, and A.D. Kelley. 1976a. Residues and persistence of glyphosate in irrigation water. *Weed Science* 24(1):47-50.
- E.P.A. 1993. Glyphosate. R.E.D. Facts. Prevention, Pesticides and Toxic Substances. EPA-738-F-93-011.
- Evans, D.D. and M.J. Batty. 1986. Effects of high dietary concentrations of glyphosate on a species of bird, marsupial and rodent indigenous to Australia. *Environmental toxicology and chemistry* 5:399-401.

- EXTOXNET. 1996. Glyphosate. Pesticide Information Profiles. Extension Toxicology Network. <http://ace.orst.edu/info/extoxnet/>.
- Feng, J.C. and D.G. Thompson. 1990. Fate of glyphosate in a Canadian forest watershed: 2. Persistence in foliage and soils. *Journal of Agricultural Food Chemistry* 38:1118-1125. Feng, J.C., D.G. Thompson and P.E. Reynolds. 1990. Fate of glyphosate in a Canadian forest watershed: 1. Aquatic residues and off-target deposit assessment. *Journal of Agricultural Food Chemistry* 38:1110-1118.
- Folmar, L. C., H. O. Sanders, and A. M. Julin. 1979. Toxicity of the herbicide glyphosate and several of its formulations to fish and aquatic invertebrates. *Arch. Environ. Contam. Toxicol.* 8:269-278.
- Forney, D.R. and D.E. Davis. 1981. Effects of low concentrations of herbicides on submersed aquatic plants. *Weed Science* 29:677-685.
- Glass, R.L. 1987. Phosphate adsorption by soils and clay minerals. *Journal of Agricultural Food Chemistry* 35(4):497-500.
- Goldsborough, L.G. and D.J. Brown. 1993. Dissipation of glyphosate and aminomethylphosphonic acid in water and sediments of boreal forest ponds. *Environmental Toxicology and Chemistry* 12:1139-1147.
- Hance, R. J. 1976. Adsorption of glyphosate by soils. *Pestic. Sci.* 7:363-366.
- Helling, C. S., P. C. Kearney, and M. Alexander. 1971. Behavior of pesticides in soil. *Adv. Agron.* 23:147-240.
- Henry, C. J., K. F. Higgins, and K. J. Buhl. 1994. Acute toxicity and hazard assessment of RodeoR, X-77 SpreaderR, and Chem-TrolR to aquatic invertebrates. *Arch. Environ. Contam. Toxicol.* 27:392-399.
- Hildebrand, L. D., D. S. Sullivan, and T. P. Sullivan. 1980. Effects of RoundupR herbicide on populations of *Daphnia magna* in a forest pond. *Bull. Environ. Contam. Toxicol.* 25:353-357.
- Liu, S., R.A. Campbell, J.A. Studens, and R.G. Wagner. 1996. Absorption and translocation of glyphosate in Aspen (*Populus tremuloides*) as influenced by droplet size, droplet number, and herbicide concentration. *Weed Science* 44:482-488.
- Lund-Hoie, K, and H. O. Friestad. 1986. Photodegradation of the herbicide glyphosate in water. *Bull. Environ. Contam. Toxicol.* 36:723-729.
- MacKinnon, D.S. and B. Freedman. 1993. Effects of silvicultural use of the herbicide glyphosate on breeding birds of regenerating clearcuts in Nova Scotia, Canada. *Journal of Applied Ecology* 30:395-406.

Glyphosate

7e.9

Malik, J., G. Barry and G. Kishore. 1989. A mini-review of "The herbicide glyphosate." BioFactors 2(1):17-25.

Marrs, R.H., A. J. Frost, R. A. Plant, and P. Lunnis. 1993. Determination of buffer zones to protect seedlings of non-target plants from the effects of glyphosate spray drift. Agriculture, Ecosystems and Environment 45:283-293.

Morrison, M.L. and E.C. Meslow. 1984. Effects of the herbicide glyphosate on bird community structure, western Oregon. Forest Science 30(1):95-106.

Neskovic, N.K. et.al. 1996. Biochemical and histopathological effects of glyphosate on carp, *Cyprinus carpio*. Bulletin of Environmental Contamination and Toxicology 56:295-302.

Newton, M. et al. 1984. Fate of glyphosate in an Oregon forest ecosystem. 32:1144-1151.

Nomura, N. S., and H. W. Hilton. 1977. The adsorption and degradation of glyphosate in five Hawaiian sugarcane soils. Weed Research 17:113-121.

Paveglio, F.L. et.al. 1996. Use of Rodeo and X-77 spreader to control smooth cordgrass (*Spartina alterniflora*) in a southwestern Washington estuary: Environmental fate. Environmental Toxicology and Chemistry 15(6):961-968.

Roberts, R.O. and S.G. Berk. 1993. Effect of copper, herbicides, and a mixed effluent on chemoattraction of *Tetrahymena pyriformis*. Environmental Toxicology and Water Quality 8:73-85.

Roslycky, E. B. 1982. Glyphosate and the response of the soil microbiota. Soil Biol. Biochem. 14:87-92.

Roy, D.N., S. K. Konar, S. Banerjee, D. A. Charles, D. G. Thompson, and R. Prasad. 1989a. Persistence, movement and degradation of glyphosate in selected Canadian boreal forest soils. Journal of Agricultural Food Chemistry 37(2):437-440.

Roy, D.N., S. K. Konar, S. Banerjee, D. A. Charles, D. G. Thompson, and R. Prasad. 1989b. Uptake and persistence of the herbicide glyphosate in fruit of wild blueberry and red raspberry. Canadian Journal of Forest Research 19:842-847.

Rueppel, M.L., B.B. Brightwell, J. Schaefer and J.T. Marvel. 1977. Metabolism and degradation of glyphosate in soil and water. Journal of Agricultural and Food Chemistry 25:517-528.

Santillo, D.J., D. M. Leslie Jr., and P. W. Brown. 1989a. Response of small mammals and habitat to glyphosate application on clearcuts. Journal of Wildlife Management 53(1):164-172.

Glyphosate

7e.10

Santillo, D.J., P. W. Brown, and D. M. Leslie, Jr.. 1989b. Response of songbirds to glyphosate-induced habitat changes on clearcuts. *Journal of Wildlife Management* 53(1):64-71.

Servizi, J. A., R. W. Gordon, and D. W. Martens. 1987. Acute toxicity of Garlon 4 and Roundup herbicides to salmon, *Daphnia*, and trout. *Bull. Environ. Contam. Toxicol.* 39:15-22.

Simenstad, C.A., et.al. 1996. Use of Rodeo and X-77 spreader to control smooth cordgrass (*Spartina alterniflora*) in a southwestern Washington estuary: 2. Effects on benthic microflora and invertebrates. *Environmental Toxicology and Chemistry* 15(6):969-978.

Sprankle, P., W. F. Meggitt, and D. Penner. 1975a. Rapid inactivation of glyphosate in the soil. 1975a. *Weed Science.* 23(3):224-228.

Sprankle, P. W. F. Meggitt, and D. Penner. 1975b. Adsorption, mobility, and microbial degradation of glyphosate in the soil. *Weed Science.* 23(3):229-234.

Sullivan, T. P., and D. S. Sullivan. 1979. The effects of glyphosate herbicide on food preference and consumption in black-tailed deer. *Can. J. Zool.* 57:1406-1412.

Thielen, K.D., E.P. Jackson and D. Penner. 1995a. The basis for the hard-water antagonism of glyphosate activity. *Weed Science* 43:541-548.

Tu, C.M. 1994. Effects of herbicides and fumigants on microbial activities in soil. *Bulletin of Environmental Contamination and Toxicology* 53:12-17.

Tyler, M.J. 1997a. Herbicides kill frogs. Newsletter of the declining amphibians population task force #21.

Tyler, M. J. 1997b. Environmentally friendly: A false sense of security? *Species.* Newsletter of the Species Survival Commission, IUCN, The World Conservation Union. 29:20-21.

WSSA. 1994. *Herbicide handbook.* Weed Society of America. Champaign, Illinois. 352 pp.

Zaranyika, M.F. and M.G. Nydandoro. 1993. Degradation of glyphosate in the aquatic environment: An enzymatic kinetic model that takes into account microbial degradation of both free and colloidal (or sediment) particle adsorbed glyphosate. *Journal of Agricultural Food Chemistry* 41:838-842.

Date Authored: April 2001

Updated: November 2001

TRICLOPYR

M. Tu, C. Hurd, R. Robison & J.M. Randall

Herbicide Basics

Chemical formula: [(3,5,6-trichloro-2-pyridinyl)oxy] acetic acid

Herbicide Family:

Pyridine (Picolinic acid)

Target Species: Broadleaf herbs and woody species

Forms: salt & ester

Formulations: EC, SL

Mode of Action: Auxin mimic

Water solubility: 430 ppm (acid), 23 mg/L (ester), 2,100,000 mg/L (salt)

Adsorption potential: Intermediate (higher for ester than salt)

Primary degradation mech:

Microbial metabolism, photolysis, and hydrolysis

Average Soil Half-life: 30 days

Mobility Potential: Intermediate

Dermal LD50 for rabbits:

>2,000 mg/kg

Oral LD50 for rats:

713 mg/kg

LC50 for bluegill sunfish:

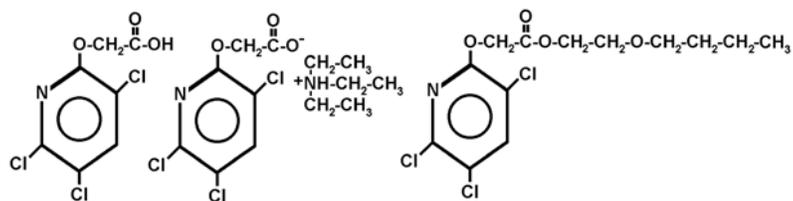
148 mg/L

Trade Names: Garlon[®] and Access[®]

Manufacturers: Dow Agro-Sciences and Platte

Synopsis

Triclopyr is a selective systemic herbicide used to control woody and herbaceous broadleaf plants along right-of-ways, in forests, and in grasslands and parklands. It has little or no impact on grasses. Triclopyr controls target weeds by mimicking the plant hormone auxin, causing uncontrolled plant growth. There are two basic formulations of triclopyr - a triethylamine salt, and a butoxyethyl ester. In soils, both formulations degrade to the parent compound, triclopyr acid. Degradation occurs primarily through microbial metabolism, but photolysis and hydrolysis can be important as well. The average half-life of triclopyr acid in soils is 30 days. Offsite movement through surface or sub-surface runoff is a possibility with triclopyr acid, as it is relatively persistent and has only moderate rates of adsorption to soil particles. In water, the salt formulation is soluble, and with adequate sunlight, may degrade in several hours. The ester is not water-soluble and can take significantly longer to degrade. It can bind with the organic fraction of the water column and be transported to the sediments. Both the salt and ester formulations are relatively non-toxic to terrestrial vertebrates and invertebrates. The ester formulation, however, can be extremely toxic to fish and aquatic invertebrates. Because the salt cannot readily penetrate plant cuticles, it is best used as part of a cut-stump treatment or with an effective surfactant. The ester can be highly volatile and is best applied at cool temperatures on days with no wind. The salt formulation (Garlon 3A[®]) can cause severe eye damage.



Triclopyr acid

Triethylamine salt

Butoxyethyl ester

Herbicide Details

Chemical Formula: [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid

Trade Names: There are two basic formulations of triclopyr: a triethylamine salt (triclopyr amine or salt), and a butoxyethyl ester (triclopyr ester). The amine formulation is sold under the trade name Garlon 3A[®] and is marketed in garden shops and hardware stores as Turflon Amine[®] or as Brush-B-Gone[®]. The ester formulation is sold under the trade name Garlon 4[®] and is marketed in garden shops and hardware stores as Turflon Ester[®]. Other trade names include Access[®], Crossbow[®], ET[®], PathFinder II[®], Redeem[®], and Remedy[®]. These products also may be mixed with picloram or 2,4-D to increase their versatility.

Manufacturers: Dow Agrosiences (formerly known as DowElanco or Dow Chemical), Platte

Use Against Natural Area Weeds: Triclopyr is used to control broadleaf herbs and woody species (WSSA 1994). It is particularly effective at controlling woody species with cut-stump or basal bark treatments. Susceptible species include the brooms (*Cytisus* spp., *Genista* spp., and *Spartium* spp.), the gorses (*Ulex* spp.), and fennel (*Foeniculum vulgare*). Triclopyr ester formulations are especially effective against root- or stem-sprouting species such as buckthorns (*Rhamnus* spp.), ash (*Fraxinus* spp.), and black locust (*Robinia pseudoacacia*), because triclopyr remains persistent in plants until they die.

Even though offsite movement of triclopyr acid through surface or sub-surface runoff is a possibility, triclopyr is one of the most commonly used herbicides against woody species in natural areas. Bill Neil, who has worked extensively on tamarisk/saltcedar (*Tamarix* spp.) control, concluded that Pathfinder II[®], a triclopyr ester formulation by DowElanco, is the most cost effective herbicide for combating saltcedar. On preserves across the U.S., triclopyr has provided good control of tree-of-heaven (*Ailanthus altissima*), salt cedar (*Tamarix* spp.), glossy buckthorn (*Frangula alnus*), common buckthorn (*Rhamnus cathartica*), sweet fennel (*Foeniculum vulgare*), Brazilian peppertree (*Schinus terebinthifolius*), and Chinese tallow tree (*Sapium sebiferum*). TNC preserves in Hawaii have successfully used triclopyr to control blackwood acacia (*Acacia melanoxylon*), bush honeysuckle (*Lonicera maackii*), Chinese banyan (*Ficus microcarpa*), corksystem passionflower (*Passiflora suberosa*), eucalyptus (*Eucalyptus globulus*), Florida prickly blackberry (*Rubus argutus*), Mexican weeping pine (*Pinus patula*), Monterey pine (*Pinus radiata*), strawberry guava (*Psidium cattleianum*), tropical ash (*Fraxinus uhdei*), and velvet leaf (*Miconia calvescens*). Triclopyr can also be used in forest plantations to control brush without significant impacts to conifers (Kelpsas & White). Spruces (*Picea* spp.) can tolerate triclopyr, but some species of pine (*Pinus* spp.) however, can only tolerate triclopyr during the dormant fall and winter months (Jotcham et al. 1989).

Mode of Action: Triclopyr is an auxin mimic or synthetic auxin. This type of herbicide kills the target weed by mimicking the plant growth hormone auxin (indole acetic acid), and when administered at effective doses, causes uncontrolled and disorganized plant growth that leads to plant death. The exact mode of action of triclopyr has not been fully described, but it is believed to acidify and “loosen” cell walls, allowing cells to expand without normal control and

coordination. Low concentrations of triclopyr can stimulate RNA, DNA, and protein synthesis leading to uncontrolled cell division and growth, and, ultimately, vascular tissue destruction. Conversely, high concentrations of triclopyr can inhibit cell division and growth.

Dissipation Mechanisms:

Summary: Both the ester and amine formulations are degraded by sunlight, microbial metabolism, and hydrolysis. In soils, both the ester and amine formulations will degrade rapidly to the parent compound, triclopyr acid. The acid and ester formulations bind well with soils, and therefore, are not likely to be mobile in the environment. The salt however, does not readily adsorb and can be mobile. The ester can be highly volatile (T. Lanini, pers. com.).

Volatilization

Ester formulations of triclopyr can be highly volatile, and care should be taken in their application. The potential to volatilize increases with increasing temperature, increasing soil moisture, and decreasing clay and organic matter content (Helling et al. 1971).

Photodegradation

Both the ester and salt formulations are degraded readily in sunlight to the parent compound, triclopyr acid, which is also photodegradable. A study of photolysis found the half-life of triclopyr acid on soil under midsummer sun was two hours (McCall & Gavit 1986). Photodegradation can be particularly important in water. Johnson et al. (1995) found triclopyr acid dissolved in water had a half-life due to photolysis of one to 12 hours.

Microbial Degradation

Microbial metabolism accounts for a significant percentage of triclopyr degradation in soils. In general, warm, moist soils with a high organic content will support the largest microbial populations and the highest rates of herbicide metabolism (Newton et al. 1990). Johnson et al. (1995a) found that microbial degradation of triclopyr was significantly higher in moist versus dry soils, and higher at 30° C than at 15° C (DT50 is 46 days versus 98 days in dry soils, and 57 days versus 199 days in moist soils, respectively). Additionally, the presence of sunlight plays a role in the rates of microbial metabolism of triclopyr. Johnson et al. (1995a) found that microbial metabolism was slowed when soil was deprived of light.

Chemical Decomposition

Hydrolysis of both the salt and ester to the acid form occurs readily in the environment and within plants (Smith 1976). McCall and Gavit (1986) reported that the ester was converted to an acid with a half-life of three hours, and that the rate of hydrolysis in water increased with an increase in pH.

Adsorption

Adsorption temporarily or permanently immobilizes triclopyr, but adsorption is not degradation. Adsorption is more important for the immobilization of the ester than of the salt formulation. The ester binds readily with the organic component of the soil, with adsorption rates increasing as organic content increases and soil pH decreases (Pusino et al. 1994; Johnson et al. 1995a). The salt form is soluble in water and binds only weakly with soil (McCall & Gavit 1986). The

strong bond between the ester and soils accounts for the relatively low mobility of the ester in soils, whereas the salt form is much more mobile (McCall & Gavit 1986). In practice, however, both compounds are degraded rapidly to triclopyr acid, which has an intermediate adsorption capacity.

Behavior in the Environment

Summary: In soils, both formulations are degraded by photolysis, microbial metabolism, and hydrolysis to the parent compound, triclopyr acid. Triclopyr acid has an intermediate adsorption potential, limiting movement of the acid in the environment. The acid degrades with an average half-life of 30 days. In water, the salt will remain in the water column until it is degraded, which can occur in as little as a few hours under favorable conditions. The ester formulation, however, is not water-soluble and can take significantly longer to degrade in water. Within plants, both the salt and ester formulations are hydrolyzed to the acid form, and transported through the plant. Residues can persist in the plant until the tissues are degraded in the environment.

Soils

Both the ester and salt formulations degrade rapidly in soils to triclopyr acid, and thereafter, behave similarly in soils. Adsorption, photodegradation, microbial metabolism, and volatility, can all play a role in the dissipation of triclopyr from soils. The reported half-life of triclopyr in soils varies from 3.7 to 314 days, but averages 30 days, depending on the formulation applied and the specific soil and environmental conditions. If soil conditions are warm and moist, microbial metabolism can be the primary means of degradation (Newton et al. 1990).

Johnson et al. (1995a) reported an average half-life of triclopyr acid in four laboratory soils of 138 days, but this time varied significantly with soil temperature. At 15°C half-lives ranged from 64-314 days, while at 30°C half-lives were 9-135 days (Johnson et al. 1995). In Southwest Oregon, Newton et al. (1990) found 24-51% of triclopyr residues remained after 37 days in a dry and cool climate. Following an increase in warmth and moisture, however, dissipation increased dramatically and triclopyr residues exhibited a half-life of 11-25 days. In a study of triclopyr persistence in soil and water associated with rice production, triclopyr had a half-life of less than ten days in the three soil types tested (Johnson et al. 1995b). In a pasture near Corvallis, Oregon, the half-life of triclopyr acid was estimated to be 3.7 days (Norris et al. 1987).

Because of the importance of photodegradation and a decrease in the size of microbial populations with soil depth, triclopyr located deeper in the soil column (>15 cm) degrades more slowly than residues near the surface (Johnson et al. 1995a). Traces of triclopyr residues have been found at soil depths of 45 cm as late as 477 days after application (Newton et al. 1990). Sandy soils that are highly permeable may therefore, retain triclopyr longer. Most studies, however, found that triclopyr generally does not tend to move in significant quantities below the top 15 cm of soil (Norris et al. 1987; Newton et al. 1990; Stephenson 1990; Johnson et al. 1995a).

Water

In water, the two formulations can behave very differently. The water-soluble salt is degraded in the water column through photolysis and hydrolysis (McCall & Gavit 1985). The ester, however, is not water-soluble and can be persistent in aquatic environments. The ester binds to organic particles in the water column and precipitates to the sediment layers (McCall & Gavit 1986). Bound ester molecules will degrade through hydrolysis or photolysis to triclopyr acid (Smith 1976), which will move back into the water column and continue to degrade. The rate of degradation is dependent on the water temperature, pH, and sediment content.

Triclopyr acid has an intermediate soil adsorption capacity. Thus, movement of small amounts of triclopyr residues following the first significant rainfall are likely (McCall & Gavit 1986), but further leaching is believed to be minor (Newton et al. 1990; Stephenson et al. 1990; Thompson et al. 1991). Movement of triclopyr through surface and subsurface runoff in areas with minimal rainfall is believed to be negligible (Newton et al. 1990; Stephenson et al. 1990). In southwest Oregon, Norris et al. (1987) found that neither leaching nor long-distance overland water flow contributed significant amounts of the herbicide into a nearby stream, and concluded that the use of triclopyr posed little risk for non-target organisms or downstream water users. Triclopyr can, however, enter waterways via aerial drift and inadvertent overspray. When the acid was applied to rice paddy fields, residues remained in the water column and were not found in significant amounts in the soil (Johnson et al. 1995b). Degradation in water was rapid and showed a half-life of four days.

Vegetation

Both the ester and salt formulations are hydrolyzed to the acid after entering plant tissue. The acid tends to remain in plants until they die or drop leaves and begin to decay (Newton et al. 1990). Newton et al. (1990) reported that triclopyr in evergreen foliage and twigs showed remarkable persistence. Although concentrations of triclopyr in the soil will decrease quickly and remain low through the winter, levels can rise again in the spring if a new supply of contaminated foliage falls from defoliating crowns (Newton et al. 1990). The residues of some herbicides in fruit have been shown to persist up to one month (Holmes et al. 1994). There is therefore a potential for long-term exposure of triclopyr to animal species that eat wild fruit. In non-target plants, triclopyr soil residues can cause damage via root uptake (Newton et al. 1990).

Environmental Toxicity

Birds and Mammals

Triclopyr is regarded as only slightly toxic to birds and mammals. The oral LD50 for rats is 630-729 mg/kg. The LD50s for mallard ducks and bobwhite quail are 1,698 mg/kg and 2,935 mg/kg, respectively. Newton et al. (1990) predicted that triclopyr would not be present in animal forage in doses large enough to cause either acute or chronic effects to wildlife, and concluded that the tendency for triclopyr to dissipate quickly in the environment would preclude any problems with bioaccumulation in the food chain. Garlon 3A[®] can cause severe eye damage to both humans and wildlife, due to the high pH of its water-soluble amine salt base. Care must be taken during mixing and application to prevent accidental splashing into eyes.

In a study of the potential effects of herbicide residues on forest songbirds, sub-lethal doses of triclopyr ester (500 mg/kg in the diet for 29 days) were found to cause weight loss and behavior alterations in zebra finches (Holmes et al. 1994). In a 1987 study of triclopyr metabolism using one cow, all traces of triclopyr were eliminated from the cow's urine within 24 hours, and no residues were detected in its milk or feces. This study, however, did not track whether any triclopyr was absorbed into the cow's tissues, or whether the triclopyr recovered in the urine was still active (Eckerlin 1987).

Aquatic Species

Triclopyr acid and the salt formulation are slightly toxic to fish and aquatic invertebrates. The LC50 of the acid and the salt formulation for rainbow trout are 117 mg/L and 552 mg/L, respectively, and for bluegill sunfish 148 mg/L and 891 mg/L, respectively. The ester formulation is highly toxic to fish and aquatic invertebrates, with an LC50 (96-hour) of 0.74 mg/L in rainbow trout and 0.87 mg/L in bluegill sunfish (WSSA 1994; EPA 1998). The hydrophobic nature of the ester allows it to be readily absorbed through fish tissues where it is rapidly converted to triclopyr acid. The acid can be accumulated to a toxic level when fish are exposed to sufficient concentrations or for sufficient durations.

The extent to which the toxic effects of the ester are reduced by degradation is poorly understood. Studies have shown that the ester formulation degrades rapidly to less toxic forms (Thompson et al. 1991). Kreutzweiser et al. (1994) however, has shown that there is a significant chance of acute lethal effects to fish exposed to low level residues for more than six hours. In addition, delayed lethal effects were seen in fish exposed to high concentrations for a short duration. Considering that Thompson et al. (1991) concluded that organisms subjected to direct overspray were exposed to a high level of herbicide for short periods of time while organisms downstream were exposed to low levels for longer periods, the findings of Kreutzweiser et al. (1994) are of concern.

Nevertheless, most authors including the authors of the fish mortality study have concluded that if applied properly, triclopyr would not be found in concentrations adequate to kill aquatic organisms. As a measure of precaution, however, Kreutzweiser et al. (1991) suggest that some water bodies remain at risk of lethal contamination levels including shallow and slow moving water bodies where dissipation is slow, and heavily shaded streams that experience reduced photodegradation.

Other Non-Target Organisms

Triclopyr inhibited growth of four types of ectomycorrhizal fungi associated with conifer roots at concentrations of 1,000 parts per million (ppm) and higher (Estok et al. 1989). Some evidence of inhibition of fungal growth was detected in bioassays with as little as 100 ppm triclopyr. Typical usage in forest plantations, however, results in triclopyr residues of only four to 18 ppm on the forest floor (Estok et al. 1989).

Application Considerations:Application Under Unusual Conditions:

Several natural area managers have found that Garlon 4[®] and 3A[®] are effective when applied in mid-winter as a cut-stump treatment against buckthorns (*Rhamnus cathartica* and *R. frangula*). It is often easier to get to these plants when boggy soils around them are frozen. Randy Heidorn, Deputy Director for Stewardship of the Illinois Nature Preserve Commission (INPC), recommends three protocols to increase the safety of triclopyr ester application in winter:

- (1) use a mineral oil based carrier;
- (2) make sure that at the time of application, no water is at or above the ground surface, and no snow or ice is present that might serve as a route to spread the herbicide following a thaw, and;
- (3) initiate a monitoring program to assess ambient water concentrations of triclopyr ester in communities that seasonally have water at or above the ground surface with little or no discharge (i.e. bogs).

Safety Measures

The salt formulation in Garlon 3A[®] can cause severe eye damage because of the high pH of its water-soluble amine salt base. Care should be taken to prevent splashing or other accident contact with eyes.

Human Toxicology

Because studies into the carcinogenicity of triclopyr have produced conflicting results, EPA has categorized triclopyr as a “Group D” compound, or a chemical that is not classifiable as to human carcinogenicity. The salt formulation in Garlon 3A[®] can cause severe eye damage.

References

Eckerlin, R.H., J. E. Ebel, Jr., G. A. Maylin, T. V. Muscato, W. H. Gutenmann, C. A. Bache, and D. J. Lisk. 1987. Excretion of triclopyr herbicide in the bovine. *Bull. Environ. Contam. Toxicol* 39:443-447.

Estok, D., B. Freedman, and D. Boyle. 1989. Effects of the herbicides 2,4-D, glyphosate, hexazinone, and triclopyr on the growth of three species of ectomycorrhizal fungi. *Bull. Environ. Contam. and Toxic.*, 42:835-839.

Helling, C. S., P. C. Kearney, and M. Alexander. 1971. Behavior of pesticides in soil. *Adv. Agron.* 23:147-240.

Holmes, S. B., D. G. Thompson, K. L. Wainio-Deizer, S. S. Capell, and B. Staznik. 1994. Effects of lethal and sublethal concentrations of the herbicide triclopyr butoxyethyl ester in the diet of Zebra finches. *J. Wildlife Dis.* 30(3):319-327.

Johnson, W. G., T. L. Lavy, and E. E. Gbur. 1995a. Persistence of triclopyr and 2,4-D in flooded and non-flooded soils. *J. Environ. Qual.*, 24:493-497.

Johnson, W. G., T. L. Lavy, and E. E. Gbur. 1995b. Sorption, mobility, and degradation of triclopyr and 2,4-D on four soils. *Weed Sci.* 43:678-684.

Triclopyr

7k.8

Jotcham, J. R., D.E.W. Smith, and G.R. Stephenson. 1989. Comparative persistence and mobility of pyridine and phenoxy herbicides in soil. *Weed Tech.* 3:155-161.

Kelpsas, B.R. and D.E. White. no date. Conifer tolerance and shrub response to triclopyr, 2,4-D and clopyralid. Northwest Chemical Company, Salem, Oregon.

Kreutzweiser, D. P., S. B. Holmes, and D. C. Eichenberg. 1994. Influence of exposure duration on the toxicity of triclopyr ester to fish and aquatic insects. *Archives of Environ. Contam. Toxic.* 26:124-129.

McCall, P. J. and P. D. Gavit. 1986. Aqueous photolysis of triclopyr and its butoxyethyl ester and calculated environmental photodecomposition rates. *Environ. Toxic. Chem.* 5:879-885.

Newton, M., F. Roberts, A. Allen, B. Kelpsas, D. White, and P. Boyd. 1990. Deposition and dissipation of three herbicides in foliage, litter, and soil of brushfields of southwest Oregon. *J. Agric. Food Chem.* 38:574-583.

Norris, L., M. L. Montgomery, and L. E. Warren. 1987. Triclopyr persistence in western Oregon hill pastures. *Bull. Environ. Contam. Toxic.* 39:134-141.

Pusino, A. W. Liu, and C. Gessa. 1994. Adsorption of triclopyr on soil and some of its components. *J. Agric. Food Chem* 42:1026-1029.

Smith, A. E. 1976. The hydrolysis of herbicidal phenoxyalkanoic esters of phenoxyalkanoic acids in Saskatchewan soils. *Weed Res.* 16:19-22.

Stephenson, G. R., K. R. Solomon, C. S. Bowhey, and K. Liber. 1990. Persistence, leachability, and lateral movement of triclopyr (Garlon) in selected Canadian forestry soils. *J. Agric. Food Chem.* 38:584-588.

Thompson, D. G., B. Staznik, D. D. Fontaine, T. Mackay, G. R. Oliver, and J. L. Troth. 1991. Fate of triclopyr ester (Release[®]) in a boreal forest stream. *Environ. Toxic. Chem.* 10:619-632.

WSSA. 1994. *Herbicide Handbook*. Weed Society of America. Champaign, Illinois, 352 pp.

Date Authored: April 2001