# FINAL REPORT

# Element E

# Chemical Methods Only: Pesticide Characterization

Submitted to

Washington State
Department of Ecology

Submitted by

EBASCO ENVIRONMENTAL

February 1993

# NOXIOUS EMERGENT PLANT ENVIRONMENTAL IMPACT STATEMENT

Chemical Characterization Report

work performed by:

Herrera Environmental Consultants, Inc. 1414 Dexter Avenue North, Suite 200 Seattle, Washington 98109

and

Ebasco Environmental 10900 NE 8th Street, Suite 500 Bellevue, Washington 98004

February 1993

# **CONTENTS**

1.0	BACKGROU	JND INFORMATION - GLYPHOSATE	1-1
	1.1 GENE	RAL DESCRIPTION	1-1
	1.2 REGIS	STRATION STATUS	1-1
	1.2.1	Registration Labels	1-1
	1.2.2	Product Efficacy and Limitations	1-2
	1.2.3	Re-registration	1-5
	1.3 ENVI	RONMENTAL FATE AND TRANSPORT	1-6
	1.3.1	Chemical Characteristics	1-6
	1.3.2	Transport Mechanisms	1-18
	1.3.3	Field Test Results	1-19
	1.3.4	Summary of Glyphosate Environmental Fate	1-22
2.0	BACKGROU	UND INFORMATION - 2,4-D	2-1
	2.1 GENE	RAL DESCRIPTION	2-1
	2.2 REGIS	STRATION STATUS	2-2
	2.2.1	Registration Labels	2-2
	2.2.2	Product Efficacy and Limitations	2-3
	2.2.3	Re-registration	2-4
	2.3 ENVI	RONMENTAL FATE AND TRANSPORT	2-6
	2.3.1	Chemical Characteristics and Degradation Processes	2-8
		Transport Mechanisms	2-24
	2.3.3	Summary of Field Tests	2-26
	2.3.4	Summary of 2,4-D Environmental Fate	2-31
3.0	ADJUVANI	S: ENVIRONMENTAL FATE AND EFFECTS	3-1
	3.1 INTRO	DDUCTION	3-1
	3.1 ENVI	RONMENTAL FATE	. 3-2
	3.2.1	Chemical Characteristics	3-2
	3.2.2	Solubility	3-4
		Biodegradation	3-5
		Impurities	3-7
		DONMENTAL EEEECTS	2 0

3.3.1 Aquatic Toxicity	3-8
3.3.2 Mammalian Toxicity	3-10
3.4 SUMMARY	3-10
4.0 PENDING REGISTRATION FOR AQUATIC USE - TRICLOPY	R 4-1
4.1 BACKGROUND INFORMATION	4-1
4.2 ENVIRONMENTAL FATE AND TRANSPORT	4-1
4.3 ENVIRONMENTAL PERSISTENCE IN SOILS	4-2
4.4 ENVIRONMENTAL PERSISTENCE IN WATER	4-3
4.5 ENVIRONMENTAL TOXICITY	4-3
5.0 EFFICACY AND PRACTICALITY OF APPLICATION METHO	DDS 5-1
5.1 HELICOPTER	5-1
5.2 BOAT	5-3
5.3 BACK-PACK SPRAYER	5-3
5.4 WICKING	5-4
5.5 INJECTION	5-4
5.6 OTHER METHODS	5-5
6.0 REFERENCES	6-1
APPENDIX 1	
APPENDIX 2	
ADDENITY 2	

# **TABLES**

1	Physico-Chemical characteristics of glyphosate	1-7		
2	Glyphosate degradation in saline sediment at Minsmeere RSPB Reserve			
	(Roundup® applied at 20/liters/ha in a spray volume of 4,000 liters/ha)	1-10		
3	Registration data gaps for 2,4-D environmental fate	2-5		
4 Chemical structure and formula for 2,4-D formulations registered for aquat				
	use in Washington state	2-7		
5	Physical/chemical characteristics of 2,4-D formulations registered for aquatic			
	use by the Washington State Department of Agriculture	2-9		
6	Concentration of 2,4-D residues in pond components	2-30		
7	Physicochemical characteristics adjuvants used with aquatic herbicides	3-11		
8	Fish and invertebrate 96 hour LC <sub>50</sub> values for triclopyr	4-4		
9	Avian eight-day dietary LC <sub>50</sub> and acute oral LD <sub>50</sub> values for triclopyr	4-4		
	FIGURES			
1	Glyphosate and degradation metabolites identified in soil (source: Torstensson			
	1985)	1-12		
2	Sorption of glyphosate on silty-clay and sandy loam soils vs. pH (from			
	Nicholls and Evans 1991)	1-15		
3	Pathway for metabolism of 2,4-D	2-17		

# **ABSTRACT**

Glyphosate and 2,4-dichlorophenoxyacetic acid are markedly different in their modes of action, as well as toxicological and environmental fate characteristics. This report summarizes the history of use of these herbicides and presents information regarding registration status, product label, and efficiency information for the aquatic environment and a review of application techniques. The major emphasis of the report is placed upon an evaluation of the efficacy and environmental fate of the two herbicides and commonly used adjuvants. This information forms the technical basis for decision-making when considering potential future uses of the herbicides in aquatic environments.

# 1.0 BACKGROUND INFORMATION - GLYPHOSATE

#### 1.1 GENERAL DESCRIPTION

Glyphosate has been used all over the world as a non-selective post-emergent herbicide in both the agricultural and forestry industries. It is also used widely for maintaining rights-of-way and facilities. Registered since the mid-1970s and sold under a variety of trade names and formulations, glyphosate is most widely known as Roundup, a 41% solution of the isopropylamine salt of glyphosate. Roundup® also contains 15.4% polyethoxylated tallow amine surfactant, and is not registered for aquatic use. Rodeo®, a 53.5% solution of the isopropylamie salt of glyphosate, was approved for aquatic use in 1982. Rodeo® does not contain a surfactant, but nonionic surfactants are required to be added to Rodeo® before application. The surfactants used for more than 95% of the applications in Washington are Ortho X-77, R-11 and LI-700 (Gilmore, personal communication; McCacken, personal communication; Crockett, personal communication). The physical/chemical characteristics of glyphosate and its environmental fate are discussed in detail in Section 1.3.

# 1.2 REGISTRATION STATUS

#### 1.2.1 Registration Labels

The glyphosate formulation of interest in Washington registered for aquatic use is Rodeo<sup>®</sup>. Rodeo<sup>®</sup>, a 53.5% solution of the isopropylamine salt of glyphosate, is a water soluble liquid that mixes readily with water and most nonionic surfactants and is applied as a foliar spray for the control or destruction of many herbaceous or woody plants. Monsanto Company, which manufactures Rodeo<sup>®</sup>, has also issued a Supplemental Label for use of Rodeo<sup>®</sup> herbicide for control of cordgrass. The Rodeo<sup>®</sup> label and the supplemental label for Rodeo<sup>®</sup> are included in Appendix 1.

The supplemental labeling provides directions for Rodeo® application as a broadcast spray from air or ground, from hand-held and high volume equipment or using a wick or wiper. Applications using any method should be at least 6 hours before treated plants are

covered by tidewater. Rainfall or immersion within 6 hours after application may reduce effectiveness.

Label information for glyphosate (Monsanto 1990) warns that the herbicide must not be allowed to "mist, drip, drift, or splash onto desirable vegetation." Application of glyphosate is not recommended when winds are gusty or in excess of 5 mph.

Rodeo® must be used with a surfactant. Although many of the nonionic surfactants on the market can be used in a tank mix with Rodeo®, in Washington three surfactants: R-11 (Wilbur-Ellis), X-77 (Ortho-Valent), and LI-700 (Loveland Industries), account for the majority of Rodeo® applications. In fact, R-11 is estimated to be used in 90 - 95% of the applications in Washington (Gilmore, personnel communication; McCacken, personal communication). Concentrations of surfactant in spray mixtures should be from 0.25 to 0.5% of total spray volume. LI-700 appears to have favorable toxicity characteristics to R-11 and X-77 and may be grounds for resource agencies to prefer it over more toxic surfactants.

# 1.2.2 Product Efficacy and Limitations

Glyphosate is a non-selective herbicide that provides control or destruction of many herbaceous and woody plants. Rodeo®, the glyphosate formulation approved for aquatic use, moves through the plant from the point of foliage contact to and into the root system. Visible effects occur on most annual plants within 2 to 4 days, but on most perennial brush species effects may not occur for 7 days or more. Extremely cool or cloudy weather following treatment may slow the activity of glyphosate and delay visual effects of control. Visible effects are a gradual wilting and yellowing of the plant which advances to complete browning of above-ground growth and deterioration of underground plant parts. In some cases, effects may not appear for up to 4 weeks depending on the physiological state of the plants.

Glyphosate was first described by Baird et al. (1971) as a postemergence spray for the control of perennial herbaceous weeds. The early effectiveness of glyphosate in agriculture soon led to applications on perennial weeds on rangeland (Gottrup et al. 1976), ornamental shrubs and Christmas tree plantings (Ahrens 1974) and in general forestry (Sutton 1978). The first report of use in an aquatic habitat is from Welker and Riemer (1982), who used glyphosate to control an infestation of fragrant waterlily

(Nymphaea odorata) in New Jersey with application rates of 2 to 4 pounds per acre in successive growing seasons. At the Montezuma National Wildlife Refuge in central New York, Rawinski (1982) and Malecki and Rawinski (1985) reported on purple loosestrife (L. salicaria test) where they used replicated plots to test three rates of glyphosate application (1.7, 3.4, and 6.7 kg/ha) against three stages of growth (vegetative, 13 June; early flowering, 13 July; late flowering, 11 August). Results showed no significant difference in application rates, but a highly significant difference from the timing of applications. The late flowering application was the most effective with nearly 100% shoot reduction.

In the following growing season, Rawinski found that the timing of application also affected the establishment of purple loosestrife seedlings - the plots sprayed in June became reinfested with seedlings, whereas the plots sprayed in July and August were free of purple loosestrife seedlings. Furthermore, the infested plots were colonized by several species of desirable waterfowl food plants.

The overall objective when controlling invasive plants in wetland or aquatic areas with glyphosate herbicide is to spray very carefully so that the noxious plants are removed but the surrounding desirable vegetation is not harmed. If this can be accomplished most of the pest species will be removed. If an infestation is treated quickly, before the noxious plant is the dominant species, the relatively small "holes" in the vegetation following removal of the weeds will be quickly filled by other perennials precluding the establishment of noxious plant seedlings (Minnesota 1988). However, in very dense growths of purple loosestrife these "holes" could be large. Follow-up treatment for at least one more season is usually necessary since some plants will be missed, new seedlings will sprout, and a few plants will survive the initial treatment. Improper mixtures and careless application, however, invariably kills more surrounding vegetation and leads to the establishment of more weed seedlings.

Glyphosate has been used for purple loosestrife control in the Northeast and Midwest with some success, where it has become an important tool in controlling the invasion of wetlands in Minnesota and Wisconsin. Rodeo® is being experimentally used for loosestrife control in Washington. The use of herbicides has been shown to be more effective in the control of purple loosestrife than current mechanical control methods (Minnesota 1988). However, glyphosate is non-selective and may, if not carefully applied, result in increasing loosestrife density because of seed germination following the

removal of competing perennial vegetation. The use of glyphosate with selective application techniques may allow it to be used effectively with minimum damage to desirable plants.

Balogh identified parameters that significantly influence response of weeds including purple loostrife, to Rodeo®, such as herbicide solution concentration, volume of herbicide sprayed, and unknown marsh effects (Balogh 1986). Time of year of treatment was also suspected to have affected purple loosestrife's response to the herbicide, although whether response increased or declined with time was not consistent among test sites. Balogh concluded that Rodeo® has the potential to be a good controlling agent for purple loosestrife, if used at appropriate rates. His data indicate that at rates < 5.79 lbs/acre some plants will survive a single treatment.

Rodeo® is also being evaluated for the control of smooth cordgrass (Spartina alterniflora) in coastal Washington, where Spartina's invasion of Willapa Bay is of critical concern. Studies initiated by the Spartina Working Group with the assistance of the U.S Fish and Wildlife Service and the staff at the Willapa National Wildlife Refuge were begun in 1990. It was hoped that these studies would demonstrate the effectiveness of Rodeo® in Willapa Bay (Crockett 1992a). Previous studies have shown that glyphosate produces 0 to 50% effectiveness in killing spartina.

Small plot replicated studies were conducted by Monsanto to simulate broadcast aerial and hand-held spray-to-wet applications. In addition, a small clone of Spartina was treated using a hand held wiper. Initial burndown of spartina with all rates and methods was complete at 2 months after treatment with nearly 100% control. Only slight differences were evident in early summer (10 months after treatment) between the 2 and 4 quart per acre broadcast treatments and the 1% and 2% v/v spray to wet solutions. All treatments exhibited excellent over-all control including control of rhizomes. Spartina control by wiping or wicking resulted in less consistent control than broadcast applications. This may be a function of failure to treat specific stems rather than a failure to achieve control of treated stems (Crockett 1992b).

Rodeo® should be applied to emerged vegetation while it is young and actively growing. Rodeo® will not control plants which are completely submerged or which have a majority of their foliage under water.

Application of glyphosate in tidally influenced areas must take into account tidal cycles. Application at, or just prior to, the maximum low tide will be necessary to provide sufficient contact time before high tide. In the Pacific Northwest, two high tides and two low tides each day severely limit the time available for application of glyphosate for tidally influenced wetlands.

No restrictions exist on the use of treated water for irrigation, recreation or domestic purposes. However, application of Rodeo® is prohibited within 0.8 Km (0.5 mile) upstream of potable water intakes. The maximum use rate for glyphosate is 8.8 l/ha (7.5 pt/acre) for each treatment. At least 24 hours must pass before retreating a given area.

The non-selectivity of glyphosate can be a limitation, since it will destroy both desirable and undesirable plants if applied broadly. In Washington, Rodeo® and 2,4-D are sometimes mixed to take advantage of their different modes of action (McCacken 1992). Mixing a sub-lethal amount of 2,4-D with Rodeo® provides some selectivity with broadleaves (hormonal effect) but doesn't damage grasses.

An approach used on terrestrial sites in Washington is to first apply Rodeo® to well established plants, where it has an effect on mature established plants. Then the plants are burned to get rid of blooms, and when the ground is open, seed germination is encouraged. The subsequent application of 2,4-D selectively attacks broadleaves, while allowing the grasses to become established (McCacken 1992).

#### 1.2.3 Re-registration

Re-registration for glyphosate is essentially complete. The only remaining study (data gap) is the field soil dissipation study, which will probably be submitted by May 1993. The EPA review of the original field soil dissipation study indicated that it should have included deeper soil samples. The environmental fate studies which are still under review are 162-1, aerobic soil (submitted 1991); 162-4, aerobic aquatic soil (submitted 1990); and 162-3, anaerobic aquatic soil (submitted 1990). All other required environmental fate studies have been found acceptable by EPA. All of the wildlife toxicity studies have been submitted and found acceptable by EPA.

#### 1.3 ENVIRONMENTAL FATE AND TRANSPORT

This evaluation of the herbicide glyphosate examines its physical and chemical characteristics, environmental transport mechanisms, and potential for accumulation, and presents a summary of applicable field test results. Because this evaluation focuses on the control of noxious emergent aquatic plants using glyphosate, only those formulations of glyphosate registered for aquatic site use by the Washington State Department of Agriculture (WSDA 1992) are addressed here.

#### 1.3.1 Chemical Characteristics

Glyphosate is a nonselective, broad-spectrum, post-emergent, systemic herbicide typically used for the control of emergent aquatic plants, broadleaf weeds, and brush. Glyphosate, or N-(phosphonomethyl)glycine, has a molecular weight of 169.1 with an empirical molecular formula of  $C_3H_8NO_5P$  and the following chemical structure:

Glyphosate exists normally as a solid (i.e., colorless crystals) having a density of 0.5 g/cc. The melting point of the solid is  $200^{\circ}$ C, and the vapor pressure is negligible i.e.,  $7.50 \times 10^{-8}$  torr (U.S. EPA 1992). General physical and chemical characteristics of glyphosate are presented in Table 1.

Three commercial glyphosate products are currently registered and approved for use on aquatic sites within the state of Washington (WSDA 1992). These include Rodeo<sup>®</sup>, Pondmaster<sup>®</sup>, and Jan/San III<sup>®</sup>. All three products are manufactured by Monsanto Agricultural Products Company, although the latter two products are no longer commercially available (C. Davis personal communication 1992). The active ingredient in these three herbicides is the isopropylamine salt of glyphosate. The isopropylamine salt is a white crystalline solid with a molecular weight of 228.2, a molecular formula of  $C_6H_{17}N_2O_5P$ , a melting point of 200°C, and a bulk density of 1.74 (Monsanto 1992; U.S. EPA 1986b). The chemical structure of the salt is:

Table 1. Physico-chemical characteristics of glyphosate.

	Isopropylamine Salt
CAS Number	1071-83-6
Manufacturer	Monsanto
Physico-Chemical Data	
Solubility (mg/L) water	12,000 (a)
Vapor pressure	negligible (a)
рН	4.6 - 4.8 (b)
Koc (e)	24,000 (c)
Kow (f)	5.6 E-4 (d)
Specific gravity	1.17 (d)
Henry's Law Constant (m3/mol)	2 E-11 (a)
Photolysis half-life	Stable (g)
Hydrolysis half-life	Stable (g)
Bioconcentration factor	Low (g)

- a) U.S. EPA 1992
- b) Monsanto 1992
- c) Washington state pesticide database (SCS 1989)
- d) Farm Chemical Handbook
- e) Organic carbon normalized soil-water partition coefficient
- f) Octanol/water partition coefficient
- g) Reinert and Rodgers 1987

Rodeo®, containing 53.8 percent glyphosate and 46.2 percent water, is a clear, viscous solution that is colorless to light amber in color. The herbicide has a pH of 4.6 to 4.8 and is odorless, completely miscible in water, and insoluble in organic solvents. The specific gravity of Rodeo® is 1.22-1.25 g/mL. The herbicide is nonflammable; the manufacturer recommends storage at above 10°F to prevent crystallization (Monsanto 1992). Rodeo® is reported by Monsanto (1992) to be noncorrosive to stainless steel, aluminum, polyethylene, plastic, and fiberglass. It is, however, corrosive to mild steel, galvanized steel, and zinc (U.S. EPA 1986b). Rodeo® can react with containers and tanks made of these materials to produce hydrogen gas, which could flash or explode if ignited by an open flame, spark, or other ignition source (Monsanto 1985). Rodeo® reportedly produces no hazardous decomposition products, nor does hazardous polymerization occur. Rodeo® can react with bases to liberate heat through chemical neutralization resulting from an acid-base reaction.

### Mode of Toxicity

When glyphosate is applied in conjunction with a surfactant to the foliage of actively growing plants, it is rapidly absorbed and translocated throughout the plant tissues. Thus, leaves, stems, and roots are affected. The translocated glyphosate is reported by Monsanto (1985) to not be broken down within the plant nor metabolized by the plant to any significant degree.

Glyphosate reportedly affects photosynthesis, respiration, and the synthesis of nucleic acids in plant tissue. The primary mode of toxicity is hypothesized to be a disruption of aromatic amino acid (phenylalamine, tyrosine, and tryptophan) synthesis and phenolic compound metabolism. This process leads to reduced protein synthesis within the plant, resulting in growth cessation, cellular disruption, and eventually death of the plant (Shaner and Lyon 1980; U.S. DOI 1992; Monsanto 1985). Depending upon the target species, the herbicidal response of glyphosate is somewhat variable. Typically, 20 to 30

percent of glyphosate applied to leaf vegetation is absorbed within 12 hours after application (Garnett 1991).

# **Solubility**

The solubility of glyphosate acid or isopropylamine salt in water at 25°C is 1.2 percent, or 12 g/L. It is insoluble in organic solvents such as ethanol, acetone, and benzene (U.S. EPA 1986b) (see Table 1).

# **Photolysis**

Glyphosate is resistant to photolysis. It remains stable in water exposed to sunlight at pH 5, 7, and 9 at temperatures between 14.7°C and 28.6°C. Its calculated half-life under these conditions is greater than 410 days (U.S. EPA 1992). The half-life of glyphosate in irradiated sandy-loam soil is 90.2 days, versus 96.3 days in nonirradiated soils (U.S. EPA 1992).

Studies of glyphosate solutions in a photoreactor revealed no alteration in the initial concentration of glyphosate (170 ppm) after irradiation of 8 hours per day for 16 days (Rueppel et al. 1977).

#### **Hydrolysis**

Pure glyphosate is stable at a pH of 3, 6, and 9 (U.S. EPA 1992) and has been shown by Brønstad and Friestad (1985) to remain stable for many years at room temperature when dissolved in distilled water or in a 1 normal solution of hydrochloric acid, indicating that the tendency for hydrolytic breakdown is low or nonexistent.

### **Degradation Products**

The principal degradation product formed from the breakdown of glyphosate is aminomethylphosphonic acid, or AMPA (Rueppel et al. 1977). AMPA also biodegrades in the soil but at a slower rate than glyphosate (see Table 2), thus resulting in accumulation in some soils (Rueppel et al. 1977).

Table 2. Glyphosate degradation in saline sediment at Minsmere RSPB Reserve. (Roundup® applied at 20 liters/ha in a spray volume of 4,000 liters/ha).

Days after Treatment	Glyphosate (mg/kg)	Aminomethylphosphonic acid (mg/kg)
0	2.6	0.1
1	1.3	0.1
7	2.8	0.4
30	1.4	0.3
360	0.5	0.2

Source: O'Keefe, M.G. 1985. The evaluation of glyphosate degradation in a bird sanctuary. Monsanto internal report (as cited by Garnett 1991).

The biodegradation of glyphosate in soil also produces other minor metabolites, but these represent less than 1 percent of the glyphosate applied (see Figure 1). These include N-methyl-aminomethylphosphonic acid, glycine, N,N-dimethylaminomethylphosphonic acid, and hydroxymethylphosphoric acid. End products of the microbial degradation of glyphosate also include carbon dioxide, water, phosphate, and nitrate (Tooby 1985).

A maximum concentration of 0.21 ppm AMPA was observed in sandy loam soil studies in Iowa, while in aerobic aquatic studies the concentration of AMPA increased with time to 23 percent of the radiolabeled percent glyphosate applied (U.S. EPA 1992). Aerobic soil studies have shown levels of AMPA at day 14 to reach 26 to 28 percent of the parent glyphosate applied. The measurement of radiolabeled carbon dioxide (CO<sub>2</sub>) evolved after 12 months in these studies amounted to approximately 71 percent of the theoretical maximum applied.

Anaerobic aquatic studies of AMPA showed 31 percent of the applied concentration remaining at day 15, and 14 to 24 percent remaining at up to 365 days. The amount of CO<sub>2</sub> evolved from the degradation of glyphosate was 35 percent of that applied after 1 year. Aerobic aquatic studies showed 19 to 25 percent of that applied remaining after 7 to 30 days. CO<sub>2</sub> evolved was 23 percent of the initial concentration after 30 days (U.S. EPA 1992).

#### Biodegradation

The degradation of glyphosate occurs aerobically or anaerobically through the action of microorganisms present in soil, water, hydrosoil, and activated sludge (Sprankel et al. 1975b; Quilty and Geoghgan 1976; Rueppel et al. 1977; Torstensson and Aamisepp 1977; Balthazar and Hallas 1986). Such microflora typically include bacteria, fungi, algae, and protozoans. Because these organisms are indigenous to water and soil environments, similar degradation processes take place in soil/water and wetland/water habitats where glyphosate use is proposed.

Aqueous biodegradation half-lives of glyphosate in field and laboratory studies are reported to range from 2 to 15 days (Hunter et al. 1984; Sacher 1978) and from 7 to 10 weeks in nonflowing natural freshwater ponds and wetland systems (Ghassemi et al. 1981).

Figure 1. Glyphosate and Degradation Metabolites Identified in Soil (Source: Torstensson 1985).

1. 
$$HO - CH_2 - N - CH_2 - P - OH$$

2. 
$$\mathbf{H} - \mathbf{N} - \mathbf{CH}_2 - \mathbf{P} - \mathbf{OH}$$
  
 $\mathbf{H} - \mathbf{OH}$ 

3. 
$$H_3C - N - CH_2 - P - OH$$
H OH

4. HO 
$$-\stackrel{\text{O}}{\overset{\parallel}{\overset{\parallel}{\parallel}}}$$

5. 
$$H_3C - N - CH_2 - P - OH$$
 $CH_3 - OH$ 

6. 
$$HO - CH_2 - P - OH$$

N-(phosphonomethyl)glycine (glyphosate)

Aminomethylphosphonic acid (AMPA)
N-methylaminomethylphosphonic acid
Glycine
N,N-dimethylaminomethylphosphonic acid

Hydroxymethylphosphonic acid

U.S. EPA (1992) pesticide fate summary data indicate that glyphosate has a half-life of 7 days in aerobic silty, clay-loam sediment. Anaerobic aquatic metabolism is slower, with a half-life of 5 weeks at pH 4.2 and 7 weeks at pH 6.3.

Depending on the soil type, the rate of glyphosate degradation is variable and dependent upon the level of microbial activity in the soil (Muller et al. 1981) or the strength of adsorption, which regulates the availability of the herbicide for degradation (Torstensson 1985). The U.S. EPA (1992) reports that glyphosate exposure to aerobic soils containing indigenous microflora results in rapid biodegradation, with a half-life of less than 1 day in sandy-loam soils and a half-life of 1 to 3 days in silty-loam soils. Sacher (1978) reports the half-life of glyphosate to vary from 3 to 27 days depending on the soil type, with almost complete biodegradation occurring in 112 days.

Persistence studies of glyphosate by Muller et al. (1981) in Finnish agricultural fields revealed that, after observations lasting 249 days over the winter period, concentrations of glyphosate decreased to levels of 10 to 53 percent of the initial (17 mg/kg) concentration in loam and silt soils, respectively. Mean monthly air temperatures during the study ranged from 10.3°C to —12.0°C. pH in the two soils was 5.1 to 5.5 while organic carbon was 44 and 1.5 percent in the loam and silt, respectively. The researchers note that no significant accumulation of AMPA occurred (maximum of 3.2 mg/kg) and that glyphosate was degraded even at low temperatures. Soil respiration activity was positively correlated with the rate of glyphosate degradation. Soil nitrification, denitrification, and nitrogen fixation activity were not affected by the application of glyphosate to these soils.

Studies of glyphosate persistence in Canadian forest soils (Feng and Thompson 1990) indicate that residues of glyphosate dissipated to 13-18 percent of initial levels (31-40 mg/kg) within 360 days of initial application. The estimated time to 50 percent dissipation was 45-60 days.

Studies have examined the potential for the formation of nitrosoamines in aerobic soils treated with glyphosate. Some nitrosoamines may cause carcinogenic, mutagenic, and teratogenic effects and toxicity at low levels. Khan and Young (1977) demonstrated that when different soils were treated at 25°C with sodium nitrate and glyphosate at high rates (20 mg/kg and 740 mg/kg, respectively), the formation of N-nitrosoglyphosate occurred (i.e., <1 ppm in Granville sandy loam to 20 mg/kg in Fox sandy loam soils). Clay

content of these soils was 20.0 and 5.1 percent, respectively. The researchers note that the high levels of glyphosate employed in these experimental conditions are not likely to be encountered in typical agricultural applications. Furthermore, treatment of these soils with typical application levels of glyphosate (5 mg/kg) and sodium nitrate (2 mg/kg) did not result in the formation of N-nitrosoglyphosate. Khan and Young state that at these levels of application they cannot envisage the formation of N-nitrosoglyphosate in soil.

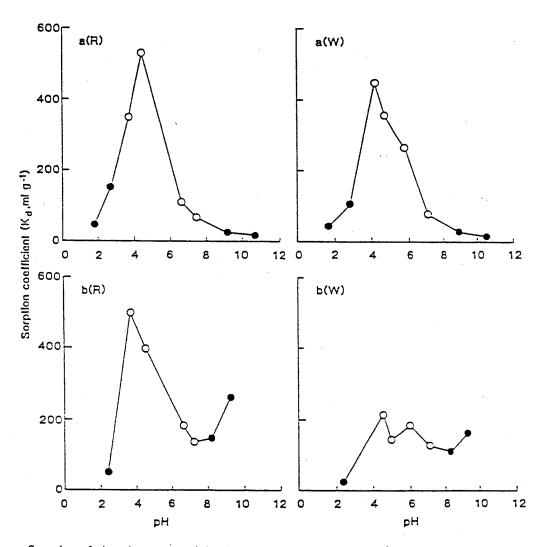
No information is currently available on the anaerobic metabolism of glyphosate in soils.

# Soil Adsorption

Glyphosate adsorbs strongly to soil particles (Sprankle 1974), and thus its leachability through soil is generally low (Torstensson 1985). Soil adsorption of glyphosate is correlated with the unoccupied phosphate sorption capacity of the soil. This binding to soil particles occurs rapidly within the first hour, decreasing slowly thereafter (Sprankle et al. 1975b). Glyphosate binding to soils is strongest in soils having low pH, high organic matter, and the highest phosphate-binding capacity (Ching et al. 1975). Soil pH was reported earlier by some researchers to have little effect on adsorption of glyphosate (Sprankle et al. 1975a, 1975b). However, recent studies of field soils indicate that the sorption of glyphosate shows a strong dependence on soil pH. Nicholls and Evans (1991) have demonstrated that glyphosate is sorbed very strongly at pH values near 4.0. This very strong sorption is attributed to ligand exchange interactions which occur over a wide range of soil pH values. Figure 2 demonstrates the variability of the sorption of glyphosate on silty-clay and sandy loam soils as a function of soil pH.

Adsorption studies of glyphosate in nine different soil types indicate that glyphosate adsorption is correlated with unoccupied phosphate sorption capacity of the soil, thus suggesting that inorganic phosphate competes with glyphosate for sorption sites in the soil (Hance 1976). Hance (1976) has concluded that the low activity (phytotoxicity) of glyphosate in soil is a result of the combination of moderate adsorption and low intrinsic toxicity of the herbicide when made available to the root system of plants.

 $R_f$  (soil mobility) values have been developed by Helling (1971) using thin-layer chromatography to evaluate pesticide mobility in soils. As soil pH increases, so do  $R_f$  values. The following  $R_f$  values describe general soil mobility:



Sorption of phosphorus-containing ions by silty-clay (R) and sandy loam (W) soils at different pH values. (a) Glyphosate. (b) Inorganic phosphate. Closed symbols are for soils where pH was adjusted by adding hydrochloric acid or calcium hydroxide solution.

Figure 2. Sorption of glyphosate on silty-clay and sandy loam soils vs. pH (from Nicholls and Evans 1991).

# R<sub>f</sub> Mobility

0.0-0.09 Immobile

0.10-0.34 Low mobility

0.35-0.64 Intermediately mobile

0.65-0.89 Mobile

0.90-1.0 Very mobile

 $R_f$  values for glyphosate ranging from 0.04 to 0.20 were observed by Sprankle et al. (1975b). Based on these values, glyphosate would be considered practically immobile in soil. Rueppel et al. (1977) reported  $R_f$  values of 0.09 to 0.18 for glyphosate and classified the herbicide as immobile in soil.

AMPA, the primary degradation product of glyphosate, was classified as slightly mobile by Rueppel et al. (1977). Runoff studies of glyphosate summarized by Brønstad and Friestad (1985) also indicate that the mobility of glyphosate in soil is low. Studies of glyphosate applied to Canadian boreal forest soils indicate no evidence of lateral movement through subsurface flow (Roy et al. 1989).

Soil-water partition coefficients (Kd) identified for glyphosate (U.S. EPA 1992) show the following soil type variation: Drummer silt-clay-loam, 62; Roy silt, 90; Spinks sandy-loam, 70; and Lintonia sandy-loam, 22. Generally, compounds with Kd values less than 5 are considered highly mobile in soil. Thus, glyphosate is generally considered to have very low mobility in soils.

In freshwater sediments, glyphosate is reported to be fairly immobile, being rapidly adsorbed by cations, in the first hour after application (Torstensson 1985; Brønstad and Friestad 1985).

#### **Environmental Half-Lives**

The U.S. EPA (1992) reports that field dissipation studies of glyphosate in loam-sand and silt-clay-loam soils indicate a 50 percent dissipation in less than 1.5 weeks and 3 weeks, respectively. Dissipation of glyphosate in forest soils in Michigan and Georgia indicate a half-life of less than 1 day; in Oregon, less than 14 days. Glyphosate or its primary degradation product AMPA did not leach into the soil below a depth of 6 inches.

The dissipation rate of glyphosate in flowing water was examined by Comes et al. (1976) in two irrigation canals located in the Yakima Valley, Washington. At application rates ranging from 1.7 to 2.2 kg/ha (1.5 to 1.95 lb/ac), glyphosate loss was reported to be 28 to 30 percent in the initial 1.6 km of each canal, with only about an additional 12 percent loss in the next 6.4 km to 12.8 km. The reason for the observed difference in loss was unknown. Initial glyphosate concentrations ranged from approximately 130 mg/L to 160 mg/L. Canal flow rates ranged from 1.7 m³/sec to 2 m³/sec, and water temperature ranged from 9°C to 12°C. The researchers state that dilution alone did not account for the reduction in glyphosate concentrations observed and cite the need for additional studies to identify those factors responsible for the glyphosate loss pattern observed.

Laboratory studies by Rueppel et al. (1977) indicate that the dissipation of glyphosate was nearly 90 percent after 14 days in Ray silt loam soils and after 80 days in Drummer silt—clay—loam soils. Soil temperatures ranged from 26°C to 32°C during the study. The half-life of glyphosate in Ray and Drummer soils at 4 mg/kg was 3 days and 27 days, respectively; at 8 mg/kg the half-life was 3 days and 25 days, respectively. These results suggest that the rate of glyphosate degradation is independent of the initial concentration, although higher rates of application were not examined in this study. Others report that the half-life of glyphosate ranges from 2 to 10 weeks in biologically active soils and hydrosoils where microbial degradation occurs (Tooby 1985).

The dissipation of glyphosate was observed to be rapid in four small Canadian (Manitoba) boreal forest ponds ranging in depth from 0.25 meters to 1.5 meters (Goldsborough and Beck 1989). The half-life of glyphosate in water ranged from 1.5 days to 3.5 days based on an initial application rate of 0.89 kg active ingredient per hectare (0.79 lb/ac) for each freshwater pond. While water temperature of the ponds was not measured, other physico-chemical properties were recorded during the August 1986 study: specific conductance, 44-502 uS/cm (at 25°C); pH, 7.0-8.1; alkalinity, 20-260 mg/L. Samples of pond water collected in the spring of the year following the glyphosate treatment did not contain detectable glyphosate.

U.S. EPA (1992) pesticide fact sheet data for glyphosate indicate that dissipation studies in pond water show a half-life of 14 to 21 days with no glyphosate detectable after 129 days. Pond sediment concentrations of glyphosate increased from 190  $\mu$ g/kg at day 7 to 6,800  $\mu$ g/kg at day 127.

#### Accumulation in Plants

The U.S. EPA (1992) reports the following accumulation of glyphosate in rotational crops: 0.028 mg/kg to 0.108 mg/kg in lettuce; 0.018 mg/kg to 0.051 mg/kg in carrot tops, and 0.0096 mg/kg to 0.037 mg/kg, roots. This accumulation was based upon an application rate of 3.71 pounds of active ingredient per acre (4.6 kg/ha) measured at 30, 119, and 364 days after treatment. Residues in 4-week-old soybeans grown in soils treated at 4 mg/kg glyphosate ranged from 0.76  $\mu$ g/kg to 4.12  $\mu$ g/kg. Soil residues during the growing period ranged from 0.64 mg/kg to 3.72 mg/kg.

#### Bioaccumulation

The U.S. EPA (1992) reports that the glyphosate bioconcentration factor in bluegill sunfish exposed to 12 ppm for 35 days is 0.38 in edible tissue, 0.63 in nonedible tissue, and 0.52 in whole fish.

Sacher (1978) conducted fish metabolism studies with glyphosate and reported a bioconcentration factor of less than 0.18. Fourteen-day exposure studies to 10 mg/L glyphosate in three fish species (channel catfish, largemouth bass, and rainbow trout) resulted in maximum whole tissue concentrations of 0.55 mg/kg, 0.12 mg/kg, and 0.11 mg/kg, respectively.

Marine mollusks (*Rangia cumenta*) exposed for 35 days to an initial water concentration of 0.54 mg/L glyphosate exhibited an average soft tissue concentration of 2.4 mg/kg following a 42-day depuration period (Heydens 1991). The maximum bioconcentration factor for soft mollusk tissues was reported to be 9.6, suggesting no significant bioconcentration of glyphosate in marine mollusks. Similar studies were conducted with crayfish (*Procambarus simulans*). After exposure for 28 days to an initial concentration of 0.53 mg/L glyphosate, and following a 44-day depuration period, the average concentration of glyphosate in edible tissue was 0.052 mg/kg, yielding a bioconcentration factor of 0.27 (Heydens 1991).

# 1.3.2 Transport Mechanisms

This section describes the potential transport of glyphosate via groundwater, surface water, and air.

#### Groundwater

Because glyphosate binds strongly with soil particles and has not been shown to leach, the potential for groundwater contamination is low. There are presently no studies demonstrating the contamination of groundwater by glyphosate.

# Surface Water

Glyphosate is soluble in water and therefore may be transported via runoff or direct contact with surface waters. Direct application of glyphosate to surface waters may result in the direct export of this material from the site. Precipitation or irrigation of an application site may result in runoff that is contaminated with glyphosate (Edwards et al. 1980). Product label information (Monsanto 1990) indicates that if rainfall or irrigation occurs within 6 hours of application, the effectiveness of the herbicide may be reduced.

### <u>Air</u>

Glyphosate exhibits a negligible vapor pressure, and therefore transfer from water to the atmosphere is also negligible. Thus, effects due to volatilization on other plants or agricultural crops are not expected. However, wind drift and spray losses of glyphosate during application may occur.

### 1.3.3 Field Test Results

Field studies investigating the application of glyphosate to aquatic systems are limited. This section summarizes the results of those studies that have examined the fate of glyphosate when applied to aquatic systems or to uplands subject to runoff. Some of these field studies have been conducted in the Pacific Northwest, while others were conducted in latitudes where climatic conditions may be considered at least comparable to those in the Pacific Northwest.

Studies by Kroll (1991) examined the fate and transport of glyphosate used to control *Phragmites* in a tidal marsh system (i.e., Fishing Bay, Maryland). Following low-tide glyphosate application to isolated patches of *Phragmites* at two tidal marsh sites, little or no glyphosate (≤5 ppb) was observed to be transported away from the application areas. The glyphosate application rate varied between 47 and 58 ounces of active ingredient per

acre (3.6-4.5 kg/ha; 3.21-4.02 lb/acre). When applied directly at the same rate to adjacent tidal ponds, glyphosate, or its primary metabolite, AMPA, was not observed to persist in the ambient pond water. These observations were made during October 1989 through January 1990. During this time water temperatures steadily decreased from approximately 23°C to 1°C.

Highly variable persistence in tidal marsh sediments and *Phragmites* thatch was observed, ranging from 348  $\mu$ g/kg to 1,273  $\mu$ g/kg through 91 days in sediment and thatch, respectively. The results for the tidal-marsh sediments were unexpected, and Kroll (1991) reports that while rapid microbial degradation was anticipated for glyphosate in the estuarine sediments, the results of this field study indicate that glyphosate can persist in certain tidal pond sediments.

Degradation of glyphosate in saline sediments has been studied, and results indicate that while breakdown occurs (see Table 2), the herbicide tends to persist even up to 1 year (O'Keefe 1985). These studies, following application of glyphosate for the control of *Scirpus moritimus* in saline mudflats, resulted in initial residues of 2.6 mg/kg glyphosate in the top 5 cm of sediment. Half-life of the residue was 30 days. Tidal effects were said to likely increase the rate of herbicide dissipation through dilution.

Similar results were obtained by Torstensson et al. (1989) in studies of Swedish soils where the average accumulation of AMPA was observed to be 8 percent of the theoretical maximum applied (i.e., 2 kg active ingredient/ha; 1.78 lb/acre) after 2 years. This occurred in forest soils located at the arctic circle, while forest soils in more temperate regions of Sweden contained only 1 percent of the theoretical maximum applied AMPA after 1 year.

Three-year field studies at the North Appalachian Experimental Watershed (Edwards et al. 1980) examined the transport of glyphosate in runoff. These studies showed that the greatest export of applied glyphosate was 0.165 kg/ha (0.147 lb/acre) or 1.85 percent of the amount applied. Typically, transport in runoff was less than 1 percent of that applied. The concentration of glyphosate in runoff was influenced by the application rate and time elapsed between herbicide application and runoff (i.e., precipitation event). At normal use rates (1.12-3.36 kg/ha; 1.0-3.0 lb/acre), runoff was affected for less than 2 months when levels decreased to <2 mg/L. At the highest application rate (8.96 kg/ha; 8.0 lb/acre), glyphosate was detected at  $5,200 \mu \text{g/L}$  in runoff and at  $2 \mu \text{g/L}$  in runoff 4

months after treatment. At normal use rates, the maximum concentration of glyphosate in runoff was less than 100  $\mu$ g/L.

Studies by Goldsborough and Beck (1989) examined the dissipation of glyphosate applied to the water surface of four small Canadian boreal forest ponds and six *in situ* microcosms over periods up to 255 days. Glyphosate added at a rate of 0.89 kg of active ingredient per hectare (0.79 lb/acre) was shown to dissipate rapidly from all ponds, with half-lives ranging from 1.5 days to 3.5 days. Glyphosate (2.5 kg/ha as Roundup®) remained at or above treatment levels in those microcosms containing only water but decreased rapidly (mean half life of 5.8 days) in those with sediment. Levels of AMPA were consistently low in ponds (<2.2 mg/L) and microcosms (<20 mg/L). Glyphosate residues in sediments of the treated microcosms generally increased over a 30-day period (i.e., maximum increases of 0.02 to 0.06 mg/kg). These results confirm the rapid dissipation of glyphosate from surface waters of lentic systems and suggest that sediment adsorption or biodegradation represent the major losses of glyphosate from the water column.

Feng et al. (1990) studied glyphosate and AMPA residues in oversprayed and buffered streams on the west coast of Vancouver Island. Maximum glyphosate residues were observed in two intentionally oversprayed tributaries (stream water, 162  $\mu$ g/L; sediments, 6.80 mg/kg dry weight; suspended sediments,  $< 0.03 \mu g/L$ ). These levels dissipated to  $<1 \mu g/L$  within 96 hours after application. Glyphosate residues were primarily associated with stream sediments rather than the stream water, suggesting that sediments act as a primary sink for these compounds. While trace levels of glyphosate (<1  $\mu$ g/L) were detected occasionally in the main stream channel and two oversprayed tributaries, no quantifiable residues ( $<1 \mu g/L$ ) of glyphosate or AMPA were detected in any stream water samples associated with storm events. Also, biweekly samples from the main stream channel and tributaries during the long-term monitoring period (196-364 days) did not show the presence of detectable residues (limits of detection =  $0.1 \mu g/L$ ) after treatment. Glyphosate and AMPA residues in bottom sediments ( $< 0.1-1.92 \mu g/g$ ) were persistent compared to stream water residues ( $<0.1 \mu g/L$ ) but declined over time so that residue concentrations were  $< 0.2 \mu g/g$  by the end of the long-term monitoring period (i.e. day 196-364).

Studies of the persistence, movement, and degradation of glyphosate in Canadian forest soils were conducted after the addition of glyphosate (Roundup®) at a rate of 2 kg of

active ingredient per hectare (1.8 lb/acre) (Roy et al. 1989). Soils at three depths (surface organic layer [SOL], SOL-15 cm, and 15 cm-30 cm) were analyzed for glyphosate and AMPA. More than 95 percent of the total herbicide residue (ranging from 707  $\mu$ g/g at day 0 to <0.05  $\mu$ g/g at day 691 and 762) was present in the upper organic layer throughout the study period (762 days). No evidence of lateral movement of glyphosate in runoff water or through subsurface flow was observed.

Newton et al. (1984) examined glyphosate herbicide residues and metabolites in Oregon forest foliage, litter, soil, stream water, sediments, and wildlife for 55 days following aerial application (3.3 kg/ha; 2.94 lb/acre). The half-life of glyphosate observed in forest foliage and litter ranged from 10.4 to 26.6 days and was twice as long in forest soils. Forest stream concentrations reached a maximum of 0.27 mg/L and decreased to below detection after 7 days. Sediment concentrations (0.55 mg/kg) were higher than water concentrations and persisted up to 55 days (0.15 mg/kg) or more. AMPA was observed at low levels in stream sediment (0.10 mg/kg) and to below detection within 55 days.

Detectable amounts of glyphosate did not accumulate in coho salmon fingerlings. All species of mammalian herbivores, carnivores, and omnivores examined had visceral and body contents of glyphosate at levels below those observed in groundcover and litter, indicating no accumulation at higher trophic levels.

# 1.3.4 Summary of Glyphosate Environmental Fate

The scientific literature indicates that glyphosate may degrade or dissipate fairly rapidly in the environment. However, degradation occurs almost exclusively through biological activity (i.e., biodegradation) and is thus dependent upon factors governing microbial activity in soil and water (i.e., temperature, moisture, pH, etc.). Thus, glyphosate may persist longer in some environments.

The half-life of glyphosate in soil and water varies considerably. The half-life in soil ranges from less than 1 day to greater than 249 days but averages about 60 days (Reinert and Rodgers 1987). The half-life in freshwater ranges from 1.5 to 21 days (Goldsborough and Becks 1989, U.S. EPA 1992), and <2 days in estuarine waters (Kroll 1991). Studies (O'Keefe 1985) have demonstrated the persistence of glyphosate (up to 1 year) in some estuarine sediments. Freshwater stream studies (Feng et al. 1990; Newton et al. 1984) have demonstrated that glyphosate and AMPA residues in bottom

sediments are persistent when compared to stream water residues, but decrease to below detection over the course of a few months.

Glyphosate is considered practically nonmobile in soils and sediments by virtue of its rapid and strong adsorption onto soil particles (Sprankle 1974). Thus its leachability through soil is generally low (Torstensson 1985). The soil mobility of glyphosate, as measured by R<sub>f</sub> values and soil partition coefficients, is very low (Helling 1971). Soil sorption of glyphosate occurs over a wide range of soil pH values (Nicholls and Evans 1991).

Groundwater contamination by glyphosate has not been reported in the literature. Soil studies (Roy et al. 1989) have demonstrated that more than 95 percent of the total herbicide residue is present in the upper soil organic layer and that the lateral movement of glyphosate in runoff or through subsurface flow was not observed. Based on the physico-chemical characteristics of glyphosate, the possibility for groundwater contamination appears remote.

Glyphosate is considered to be nonvolatile and therefore to have a low potential for damage to nontarget species when used adjacent to agricultural croplands. However, wind drift and spray losses may carry the applied product to non-target plants. Washoff of the herbicide from rainfall or irrigation of treated plants within 2 hours of application may render the treatment ineffective and at the same time disperse the herbicide into the environment.

# 2.0 BACKGROUND INFORMATION - 2,4-D

#### 2.1 GENERAL DESCRIPTION

The chlorinated phenoxyacetic acids and their derivatives, which include the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), are among the most widely used pesticides in the world. The active ingredient 2,4-D acid was one of the first pesticides to be registered in the U.S. and is still a commonly used herbicide for controlling broadleaf weeds. Although production of 2,4-D and other phenoxyacetic acids are decreased sharply in the late 1960s because of reduced Vietnam usage, U.S. production figures in the 1970s suggested that this downtrend was reversed (U.S. EPA, 1972).

There are over 1,000 registered pesticide products that contain one or more 2,4-D, its structural analogs 2-(2,4-dichlorophenoxybutyric acid (2,4-DB) and 2-(2,4-dichlorophenoxypropionic acid (2,4-DP), or a salt, ester or amine derivative of the acids.

The majority of 2,4-D is used to control weeds in wheat, field corn, grain sorghum, sugarcane, rice, barley, rangeland, and pastureland. It is also used for residential and aquatic weed control, in forest management, and as a growth regulator on crops including citrus, filberts and potatoes. The acid and derivatives of 2,4-DB are used primarily to control broadleaf weeds in alfalfa, soybeans and peanuts. The major uses of 2,4-DP and its amines and esters are for weed control in turf, on non-bearing citrus, on rights of way and in forestry.

2,4-D is used for aquatic applications, particularly throughout the southeastern and western United States (K. Getsinger, personal communication 1992). Tennessee Valley Authority and the Army Corps of Engineers have used 2,4-D formulations to control noxious aquatic weeds. Both liquid and granular formulations are used to control noxious aquatic weeds. Liquid formulations such as Weedar 64® are used to control surface and immersed vegetation; in the TVA system only, Weedar 64® is registered for the control of water milfoil. Granular formulations are often used to control submersed vegetation.

State resource agencies in Minnesota and Wisconsin have found 2,4-D to be an effective tool in the control of purple loosestrife in wetland areas. 2,4-D based herbicides do not harm monocot species, which are the dominant species in most wetland areas.

#### 2.2 REGISTRATION STATUS

### 2.2.1 Registration Labels

Approximately 30 2,4-D formulations are registered for aquatic use in Washington. Currently, the Department of Ecology does not currently grant permits for use of 2,4-D formulations in waters of Washington State. Any use of 2,4-D formulations must be 1 foot above mean high water line at any given site. The most commonly applied formulations for use near the aquatic environment are Weedar 64® (Rhone Poulenc), Herbicide A-4D® (Albaugh), 2,4-D Amine® (Helena), Amine 4® (Wilbur Ellis), and Amine 6-D® (Platte Chemical). These products are all amine salts of 2,4-D acid. Label restrictions and product characteristics inhibit the use of ester formulations in or near aquatic environments, as some formulations are toxic to aquatic invertebrates..

These most commonly applied products are labeled for use in ponds, lakes, reservoirs, marshes, bayous, drainage ditches, canals, rivers and streams that are quiescent or slow-moving. Label instructions for the control of annual and perennial broadleaf weeds are to treat plants when young and actively growing before bud or early bloom stage. For hard to control weeds, a repeat spray may be needed after 3 to 4 weeks for maximum results, using the same rates. When used in lakes, ponds, drainage ditches and marshes, foliage should be sprayed until thoroughly wet. Labels recommend that application be made when leaves are fully developed above water line and plants are actively growing. No more than 1/3 to 1/2 of a lake or pond must be treated at a time, and 10-14 days must be allowed between treatments. Application of 2,4-D must be limited to a portion of the water body at any one time, because decaying vegetation can deplete the oxygen content of the water. Aquatic organisms need oxygen to survive and an adequate water:oxygen ratio must be maintained.

Boom spraying onto the water surface should be kept to a minimum, and no cross-stream spraying to opposite banks is permitted. When spraying shoreline weeds, no more than a two foot over-spray onto water with an average of less than 1 foot over-spray is allowed, in order to prevent introduction of greater than negligible amounts of chemical into the

water. The environmental effects of 2,4-D in aquatic systems are addressed in the Environmental Effects Report (Ebasco 1992).

# 2.2.2 Product Efficacy and Limitations

2,4-D is a somewhat selective systemic growth regulator with hormonelike activity. It is readily translocated throughout the plant, especially from the foliage to roots. It inhibits cell division of new tissue and stimulates cell division of some mature plant tissues, resulting in growth inhibition, necrosis of apical growth, and eventually, total cell disruption and plant death.

For best results, 2,4-D herbicides should be applied in spring or early summer when young vegetation is actively growing, preferably in the bud and flowing stage of growth. Approximately 2 weeks is required for control of most vegetation; tissue damage should be evident within 2 to 4 days with liquid formulations and a week with granular formulations. Regrowth would be evident in 4-5 weeks if roots are not killed. Maximum water concentrations must not exceed 0.1 mg/l (ppm). Some labels state that treated water must not be used for irrigation, livestock watering or domestic water supplies for 3 weeks posttreatment unless an approved assay shows water does not contain more than 0.1 mg.l (ppm) 2,4-D acid. This restriction is usually found only on labels which contain specific instructions for using the product near drainage ditches, bayous, canals, rivers, streams. Other labels simply state that the product should not be allowed to contaminate any water supplies, with no qualifiers added about time restrictions. The code of Federal Regulations 180.142 establishes tolerances for negligible residues (0.1 ppm(N)) of 2,4-D from application of its dimethylaime salt to irrigation ditch banks in the Western United States.

2,4-D is generally most efficacious when used in conjunction with other herbicides and management tools to control noxious weeds. One of its chief advantages is that it is somewhat selective and will severely impact only dicots. It can be used with other herbicides, such as Rodeo®, as discussed above. It can also be used in conjunction with mechanical controls to manage invasive noxious plants. In Minnesota, Voyageaurs National Park has spot-sprayed individual purple loosestrife plants with 2,4-D twice between late June and early August. In mid-August, workers cut and bag any remaining flower stalks, remove them from the wetland and burn them. Since using this approach,

initiated in 1988, the density and age structure of the loosetrife stands in the park have dramatically reduced (Benedict, 1990).

### 2.2.3 Re-registration

2,4-D is undergoing a massive re-registration effort. The re-registration process includes generation and review of toxicity studies and implementation of exposure reduction measures. The re-registration is on track (L. Hammond personal communication 1992); new due dates for overdue studies have been established in a recently negotiated agreement between EPA and the 2,4-D task force (a group of the technical registrants), in which EPA recognized that a good faith effort by the registrants was occurring (J. Coombs personal communication 1992). Registrants also agreed to include language on the labe Idesigned to reduce human exposure to 2,4-D. The completion of all remaining toxicity studies is scheduled in the proper timeframe for submittal by December 1995. There are 68 studies remaining to be submitted; 35 studies have already been submitted to EPA for the re-registration effort. A listing of the generic data requirements for 2,4-D acid amines, and esters is provided in Table A of Appendix 2. All studies must be submitted by December 1995, or the registration for 2,4-D could be revoked.

Of the toxicity studies that have been submitted for the 2,4-D acid and ester, all of the required wildlife studies have been found acceptable. Most of the environmental fate studies for the acid have been submitted, while studies with the ester are on-going. The studies that still represent data gaps in environmental fate are shown in Table 3. The studies that have been submitted for 2,4-D acid, 2,4-D DMA Salt, and 2,4-D 2EH ester that were unacceptable are shown in Table B of Appendix 2.

In addition to the 2,4-D studies required by EPA, two epidemiologic studies sponsored by the National Cancer Institute have been completed. EPA anticipates receiving data from these studies in January 1993 and will conduct a review of weight-of-evidence carcinogen classification of 2,4-D at that time (J. Bloom personal communication 1992).

As part of the recently negotiated agreement between EPA and the 2,4-D task force, the registrants will also implement exposure reduction measures. These measures will include label changes and user education programs, such as a 2,4-D telephone hotline, brochures, and seminars (J. Coombs personal communication, 1992). The effective dates

Table 3. Registration data gaps for 2,4-D environmental fate.

Guideline Ref. No.	Study	Status
161-1	hydrolysis	acid accepted, ester in
	photodegradation	
161-2	water	in progress
161-3	soil	submitted 1989
161-4	air	waiver request
	metabolism	all are being repeated, data will be submitted in 1994
162-1	aerobic soil	
162-2	anaerobic soil	
162-3	anaerobic aquatic soil	
162-4	aerobic aquatic soil	
163-1	leaching and adsorpsion/desorption	submitted 11/91
	dissipation studies	repeating all of these, submit by 12/95
164-1	field soil	
164-2	aquatic (sediment)	
164-3	forestry	•
	accumulation studies	
165-4	fish	submit by 12/95

for these measures will be between 1993 and 1995, depending on the dates the product was formulated and sold. EPA's summary of the agreement and its specific effective dates are shown in Appendix 3.

#### 2.3 ENVIRONMENTAL FATE AND TRANSPORT

This section describes the environmental fate and transport mechanisms for the 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide. Although there are approximately 35 different registered formulations of 2,4-D (U.S. EPA 1988a), this review addresses only those formulations that are registered for aquatic use (WSDA 1992):

- 2,4-D dimethylamine salt (2,4-D DMA)
- 2,4-D butoxyethyl ester (2,4-D BEE)
- 2,4-D isooctyl (2-octyl) ester
- 2,4-D isooctyl 2-ethylhexyl ester
- 2,4-D sodium salt
- 2,4-D alkyl amine C12.

Chemical structures and formulas for these 2,4-D formulations are provided in Table 4.

The two most commonly used forms include the dimethylamine (2,4-D DMA) salt and butoxyethyl ester (2,4-D BEE) compounds. The parent, acid compound is not typically formulated as an end-use product. However, because most studies have utilized the acid and because information concerning the mobility and persistence of many of the other formulations is incomplete, the acid compound has been included in this review. In addition, the ester and amine formulations commonly used in aquatic applications are rapidly converted to acid form in the environment. Therefore, the chemical characteristics of 2,4-D acid will likely be representative of the various formulations under field conditions.

The following sections summarize available information on the chemical characteristics of each formulation that affect its environmental persistence and mobility (e.g., hydrolysis, photolysis, solubility, soil adsorption characteristics, volatilization, and biodegradation). Available field studies utilizing 2,4-D are also summarized.

Table 4 goes here

# 2.3.1 Chemical Characteristics and Degradation Processes

2,4-D is a systemic herbicide that is used to control broadleaf weeds, grasses, woody plants, aquatic weeds, and nonflowering plants. It functions as a plant growth regulator that stimulates nucleic acid and protein synthesis and affects enzyme activity, respiration, and cell division. Chemical characteristics of the 2,4-D formulations registered for aquatic use in Washington State (Washington State Department of Agriculture 1992) are summarized in Table 5.

# Solubility

The acid form of 2,4-D is a white crystalline solid with a water solubility of 600 mg/L (Reinert and Rodgers 1987) to 9000 mg/L at 20°C (U.S. EPA 1992). It has a  $K_{ow}$  ranging from 479-645 (Hunter et al. 1984; Chiou et al. 1977). The dissociation constant for the acid (p $K_a$ ) is 2.64 (Dean 1985).

The amine salt (2,4-D DMA), a white crystalline solid, is highly soluble in water, ranging from 10,000 mg/L at 2°C (U.S. EPA 1992) to 3,000,000 mg/L (Reinert and Rodgers, 1987). The ester formulations are typically insoluble in water, but are soluble in organic solvents. 2,4-D BEE, the most commonly used ester, is a colorless to amber, oily liquid. Water solubility of 2,4-D BEE is reported at 1-12 mg/L (Reinert and Rodgers 1987; U.S. EPA 1992).

#### <u>Hydrolysis</u>

Available information indicates that 2,4-D esters rapidly hydrolyze to 2,4-D acid in water and moist soil. In laboratory studies, Zepp et al. (1975) determined that the hydrolysis of 2,4-D BEE was pH-dependent with the hydrolysis half-life predicted by the following equation:

$$T(1/2) = 0.693/(K_b)[OH]$$
  
where: $K_b = \text{hydrolysis rate constant (mol}^{-1} \text{ sec}^{-1})$   
 $[OH] = \text{hydroxyl ion concentration.}$ 

Values for the rate constant vary from 30.2 mol<sup>-1</sup>sec<sup>-1</sup> at 28°C to 235 mol<sup>-1</sup>sec<sup>-1</sup> at 47°C. Based on this equation, the hydrolysis half-life for 2,4-D BEE in 28°C water at pH 9

SOW/2-2-93/03554A

Dimetry laminic   Sodium   2-Batocycety   Isoocty   Is							Page 1 of 2
Agrication   2008-39-1   2702-72-9   1929-73-3   1928-43-4   1917-97-1   94-71   94-		Dimethylamine Salt	Sodium Salt	2-Butoxyethyl Ester	Isooctyl (2-ethylhexyl) Ester	Isooctyl (2-octyl) Ester	2,4-D Acid
Nationaries (a)   Agrolinz Aquacide Co.   Rhone Poulenc   Agolinz   Agolinz   Helena   Applied   Helena   Applied   Helena   Helena   Biochemists   Wilbur-Ellis   Riverdale   Riverdale   Helena   Riverdale   Helena   Albaugh   Riverdale   Albaugh   Riverdale   Albaugh   Riverdale   Albaugh   Riverdale   Albaugh	CAS Number	2008-39-1	2702-72-9	1929-73-3	1928-43-4	1917-97-1	94-75-7
Helena   Riverside/Terra   Helena   H	Manufacturers (a)	Agrolinz	Aquacide Co.	Rhone Poulenc	Agolinz	Agolinz	( <del>p</del> )
Wilbur-Ellis   Helena   Riverdale   Riverside   Riverside   Riverside   Riverside   Riverside   Riverside   Riverside   Terra   Albaugh   Riverdale		Riverside/Terra			Helena	Applied Biochemists	
Plate   Riverside   Riverside   Conex   Helena   Riverside   Terra   Helena   Riverside   Terra   Helena   Riverside   Terra   Helena   Albaugh   Riverdale   Albaugh   Albaug		Wilbur-Ellis				Helena	
Land O Lakes/ Cenex   Helena   Helena   Helena   Helena   Helena   Helena   Albaugh   Riverdale   Riverdale   Riverdale   Helena   Riverdale   Helena   Albaugh   Riverdale   Helena   Riverdale   Helena   Riverdale   Helena   Riverdale   Helena   Helena   Riverdale   Helena   Helena   Helena   Helena   Helena   Riverdale   Helena   H		Platte				Riverdale	
Helena Albaugh Riverdale  al/Chemical Data  Albaugh Bity (mg/L water) (l) 3.0E+6 (c) 45000/25 (l) 12 (c) 300-  pressure (mm Hg) (l) 1.1E-7/38 (k) 6.0E-4_2 3E-1/25 (k) 8.0E-5-1  by Law constant (atm m3/mol) Insignificant (c) 1.0E-2-1.0/25 (k) 1.0E-2-1 3400 (c) 3400 (c) 0.13-0.25 (c) 0.19 (cid 0.1		Land O Lakes/ Cenex				Riverside/ Terra	
Riverdale   Riverdale		Helena					
Riverdale   Riverdale		Albaugh					
al/Chemical Data  ity (mg/L water) (t) 3.0E+6 (c) 45000/25 (t) 12 (c) 300-  pressure (mm Hg) (t) 1.1E-7/38 (k) 6.0E-4.2 3E-1/25 (k) 8.0E-5-1  s Law constant (atm m3/mol) Insignificant (c) 1.0E-2-1.0/25 (k) 1.0E-2-1.0/25 (k) 0.45 (loa 0.13-0.25 (c) 0.13-0.25 (c) 0.0 (sandy)		Riverdale		The state of the s			
ity (mg/L water) (l) 3.0E+6 (c) 45000/25 (l) 12 (c) 300-  pressure (mm Hg) (l) 1.1E-7/38 (k) 6.0E-4.2 3E-1/25 (k) 8.0E-5-1  s Law constant (atm m3/mol) Insignificant (c) 1.0E-2-1.0/25 (k) 1.4E-5-3  Low (c) 2.13-0.25 (c) 0.13-0.25 (c) 0.19 (c) 0.1	Physical/Chemical Data						
pressure (mm Hg) (l)  1.1E-7/38 (k)  6.0E-4.2 3E-1/25 (k)  8.0E-5-1  8.0E-5-5-5  1.0E-2-1.0/25 (k)  1.0E-3-1.0/25 (k)  1.0E-3-1	Solubility (mo/L. water) (I)	3 08+6 (c)	45000/25 (i)	12 (6)			300-9000/20 (40)
s Law constant (atm m3/mol) Insignificant (c) 1.0E-2-1.0/25 (k) 1.4E-5-3  Low (c) 3400 (c) 0.45 (loa 0.13-0.25 (c) 0.19-0.25 (c) 0.99 (loa 0.19 (cil.) 0.19 (cil.) 0.19 (cil.) 0.19 (cil.) 0.00 (sandy	Vapor pressure (mm Hg) (l)	÷		.0E-4.2 3E-1/25 (k)		8	.3E-5-1,1E-3/20 (k)
0.45 (loa 0.13-0.25 (c) 0.19-0.25 (c) 0.99 (loa 13 (loa 0.19 (loa 0.19 (cil	Henry's Law constant (atm m3/mol) Kow (d)	Insignificant (c)		1.0E-2-1.0/25 (k) 3400 (c)		1	.4E-5-5.5E-1/25 (k) 479-645 (c)
	Kd (e)	0.13-0.25 (c)				0.00	45 (loam, pH=6.5) 99 (loam, pH=5.9) 13 (loam, pH=7.8) .19 (clay, pH=7.7) (sandy loam pH=7)

SOW/2-2-93/03554A

Table 5.	Table 5. Physical/Chemical Characteristics of 2,4-D formulations registered for aquatic use by the Washington State	Characteristics of 2	,4-D formu	lations registered f	or aquatic use by	the Washington	State
	Department of Agriculture.	culture.					
							Page 2 of 2
		Dimethylamine Salt	Sodium Salt	2-Butoxyethyl Ester	Isooctyl (2-ethylhexyl) Ester	Isooctyl (2-octyl) Ester	2,4-D Acid
Koc (f)		18-20 (k)		(2) 0069-2099			330-617 (c)
Hydrolysis h Photolysis ha	Hydrolysis half-life (days (g) Photolysis half-life (days)	Insignificant (c) Insiginificant (c)		0.02-26 (h) 12 (g) 10-20 (c)	150	1500 (pH=6.0)	<30 (pH=5.0) >30 (loam soil)
Bioconcentration factor	tion factor	1-7 (c)		162-408 (c)			<10-20 (c)

Blank spaces indicate data not available

0.6-16.8 0.47-6.0

0.23-9.5 1.1-38

0.23-15.2

Terrestrial sites Aquatic sites

Application Rates (lb ae/Ac) (h)

Washington Department of Agriculture (1992)

2,4-D acid not formulated as an end-use product Reinert and Rodgers (1987)

Octanol-water partition coefficient Soil-water partition coefficient

Organic cabon normalized soil-water partition coefficient

EPA (1992)

EPA (1988a)

Shiu et al. (1990) EPA (1988b)

Balogh and Walker (1992) 

value/temperature

was estimated to be approximately 0.6 hours and at pH 6 was approximately 26 days. In comparison, the half-life for 2,4-D isooctyl ester was estimated at 37 hours (pH 9.0) and 1,500 days (pH 6.0) respectively, at 28°C. Hydrolysis typically occurs more rapidly at higher temperatures.

Hydrolysis of 2,4-D esters was also found to occur in moist soil. In soil at 25°C with moisture content above the wilting point, isooctyl esters of 2,4-D were converted to acid within about 72 hours (W. Chase personal communication 1985). However, hydrolysis was minimal in air-dried soils. Grover (1973) reported a half-life of 3.5 days at pH 5.3 in soils for the isooctyl ester.

Hydrolysis is not an important process in the degradation of the 2,4-D DMA salt. However, the amine salt rapidly dissociates (27-36 minutes) to 2,4-D acid (Dynamac 1988). Grover and Smith (1974) report that <sup>14</sup>C labeled 2,4-D DMA dissociates in moist soils and that the <sup>14</sup>C-dimethylamine cation becomes strongly sorbed to soil colloids. The soil adsorption characteristics of the amine salt are very similar to the acid form.

# **Photolysis**

Studies have shown that the various 2,4-D formulations are subject to photodegradation. In aqueous solution at pH 7, the concentration of the 2,4-D sodium salt declined by 50 percent in 50 minutes when exposed to ultraviolet radiation (wavelength 254 nm) (W. Chase personal communication 1985). Phototransformation generated 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, and 2-chloro-4-hydroxyphenoxyacetic acid as intermediate products, with polymeric humic substances as the end product. Because of the large quantity of humic substances generated, it was suggested that 1,2,4-trihydroxybenzene may also have been generated as an intermediate product. When exposed to sunlight for several days, the 2,4-D sodium salt also yielded 2,4-dichlorophenol and 2-hydroxy-4-chlorophenoxyacetic acid as intermediates and humic substances as the final reaction product.

In similar experiments with the ethyl ester of 2,4-D exposed to >290 nm wavelength ultraviolet radiation, only the corresponding esters of 2- and 4-chlorophenoxyacetic acid were generated (W. Chase personal communication 1985). These esters did not appear to undergo further degradation. No phenols were identified during the degradation process.

Zepp et al. (1975) exposed dilute (<1 mg/L) air-saturated solutions of 2,4-D BEE to ultraviolet radiation (>290 nm wavelength). Dehalogenation by-products and 2,4-dichlorophenol were reported as byproducts of the reaction. However, when higher concentrations of 2,4-D ester were used, photodecomposition yielded the respective 2-and 4-chlorophenoxyacetic acid esters. The photolysis half-life for 2,4-D BEE was estimated at 13-20 days (Zepp et al. 1975).

# **Volatilization**

Available data indicate that neither the ester (2,4-D BEE) or the amine salt (2,4-D DMA) formulations of 2,4-D are highly volatile. At 25°C, the vapor pressure of 2,4-D BEE is 4.5 x 10<sup>-6</sup> mm mercury (Zepp et al. 1975). Henry's Law constant for 2,4-D BEE is reported at 10<sup>-6</sup> to 10<sup>-7</sup> atm cubic meter/mole (Hunter et al. 1984; Thibideaux 1979). Given these characteristics, the volatilization half-life for 2,4-D BEE in an aquatic system at 25°C and 1 meter depth has been estimated at 895 days (Zepp et al. 1975). Similarly, 2,4-D DMA which has a low vapor pressure (Klingman et al. 1975) and high solubility in water would also exhibit low volatility.

2,4-D acid with a vapor pressure of  $8.0 \times 10^{-6}$  mm Hg and a Henry's Law constant of  $2.5 \times 10^{-10}$  atm cubic meter/mole is considered nonvolatile (Reinert and Rodgers 1987).

#### Soil Adsorption

Soil leaching studies indicate that 2,4-D acid is moderately to highly mobile in most soils. As a result, EPA has included 2,4-D on its list of pesticides that have a high potential for leaching to groundwater (U.S. EPA 1988a). Available information concerning the soil leaching characteristics of 2,4-D (acid form) are summarized below (Dynamac Corporation 1988):

Soil Partition Coefficient (K <sub>d</sub> )	Soil Mobility Coefficient R <sub>f</sub>
0.291	1.0
0.363	0.77
1.18	0.60
No data	0.41
12.7	No data
	Coefficient (K <sub>d</sub> ) 0.291 0.363 1.18 No data

Soil partitioning measures the potential for a chemical to be adsorbed onto soil particles. Generally, compounds with K<sub>d</sub> values less than 5, and particularly those with K<sub>d</sub> values less than 1.0 are considered to be highly mobile in soil (U.S. EPA 1986a). R<sub>f</sub> values were developed by Helling (1971) using thin layer chromatography to evaluate pesticide mobility based on the following classification system:

# $\underline{\mathbf{R}}_{\mathbf{f}}$ 0.0 - 0.09**Immobile** 0.10-0.34 Low mobility

**Mobility** 

0.35-0.64 Intermediately mobile

0.65-0.89 Mobile

0.90 - 1.0Very mobile

Based on these data, 2,4-D would be considered very mobile in sand; intermediately mobile to mobile in sandy loam, silt loam, and loam soils; and relatively immobile in clay loam.

In leaching column studies using a silt loam soil treated with aged (30 days) residues of 2,4-D acid, all 2,4-D remained in the upper 2 inches of the 12 inch column (Dynamac Corporation 1988). Columns were treated with 0.79 mg/kg C<sup>14</sup>-2,4-D acid and leached with 0.5 inches of water applied each day for a period of 47 days. No 2,4-D residues were found in the leachate. These results suggest that 2,4-D is relatively immobile in silt loam soil, in contrast with the study cited earlier that classified 2,4-D as intermediately mobile in silt loam.

Barriuso et al. (1992) conducted adsorption studies using 2,4-D acid on two Brazilian Oxisols, a highly weathered soil containing a large proportion of clay-sized particles dominated by hydrous oxides of iron and aluminum. Organic carbon content of the soils used in the study ranged from 1.28 to 4.9 percent. Soil cation exchange capacity was also low (2.9-12.6 meg/100g). Five gram soil samples were treated with 0.1 mg of 2,4-D and mixed for 24 hours. Partition coefficients (K<sub>d</sub>) ranged from 0.7 to 17.7 L/kg. K<sub>d</sub> values were highest in the soils that contained a greater concentration of iron and aluminum oxides. No correlation between K<sub>d</sub> and soil organic carbon content was identified. However, it was determined that 2,4-D adsorption was affected by soil pH. K<sub>d</sub> values were found to be inversely proportional to pH in both laboratory and field

studies. For example, the  $K_d$  value decreased from a high of about 15 L/kg at pH 4.1 to approximately 5 L/kg at pH 4.5. The lowest  $K_d$  value (<1 L/kg) was observed at pH 5.5. The researchers concluded that the variation in  $K_d$  values with pH was caused by the increase in negative charge of the organic matter and the increase of positive charge on the iron and aluminum oxides as pH decreased.

Adsorption of 2,4-D on pure clays and silts is negligible (Grover and Smith 1974; Weber et al. 1965). Harris and Warren (1964) reported a weak, reversible adsorption reaction in organic muck. Many of the degradation products of 2,4-D are similar in structure to the humic acid complexes found in sediment. Bollag et al. (1980) showed that cross coupling between the phenolic constituents of humus and 2,4-dichlorophenol (2,4-DP), one of the major byproducts of 2,4-D degradation can easily occur in the presence of an extracellular enzyme isolated from the fungus *Rhizoctonia praticola*. The oxidative coupling results in 2,4-DP being strongly bound to the organic matter. The enzyme/2,4-DP solutions used in the experiment were incubated for 2 hrs at 30°C (Bollag et al. 1980).

# **Biodegradation**

Studies have shown that 2,4-D is degraded by a variety of bacteria and fungi, including, *Pseudomonas, Arthrobacter, Flavobacterium, Corynebacterium, Achrobacter, Nocardia, Streptomyces, and Aspergillus* (Chakrabarty 1982). In soil, biodegradation occurs fairly rapidly under warm, moist conditions. Half-lives in agricultural soils of 1-2 days have been reported for the 2,4-D BEE ester and 1.5-7 days for 2,4-D residues (Grover 1973; Smith 1972 and 1978). The factors affecting soil biodegradation rates include temperature, soil moisture content, organic matter content, and soil pH (Kim and Maier 1986). Biodegradation typically occurs more rapidly in soils that have previously been exposed to 2,4-D due to the presence of organisms adapted to 2,4-D degradation.

Degradation in the surface water environment is more variable, with half-lives in water ranging from a few days to several months (U.S. EPA 1987). 2,4-D residues are also generally more persistent in aquatic sediments with 2,4-D residues remaining as long as several months (Smith and Isom 1967; Frank and Comes 1967; Cope et al. 1970; Wojtalik et al. 1971; Schultz and Harman 1974; Watson 1977; MacKenzie 1979; Mount and Stephan 1967). For example, Otto et al. (1983) reported residues of 2,4-D (<0.2 mg/kg) in hydrosoils in Fort Cobb reservoir (Oklahoma) up to 56 days after treatment

with 2,4-D BEE (Aquakleen®). In tests using an artificial pond treated with Aquakleen®, Birmingham and Colman (1985) found that the concentration of 2,4-D in pond sediments decreased from 8 mg/kg 1 day after treatment to less than 2 mg/kg by day 34. However, 2,4-D residues (0.6 mg/kg) were observed as long as 182 days after treatment. Greater persistence is reportedly caused by low oxygen and low temperatures often associated with aquatic sediments. In addition, certain formulations such as 2,4-D BEE, which is typically applied as "slow release" granular crystals may be more persistent in aquatic sediments. Granular crystals are recommended for control of aquatic macrophytes whereas purple loosestrife and other emergent vegetation are typically treated with foliage sprays (Burrill et al. 1992).

By comparison, in enriched laboratory conditions, high concentrations of 2,4-D can be broken down in a matter of hours (Shearer and Halter 1980). Kim and Maier (1986) reported that in acclimated cultures inoculated with activated sludge from a municipal wastewater treatment plant, approximately 90 percent removal of 2,4-D occurred within 120-140 hrs. The starting concentrations of 2,4-D in these experiments ranged from 10-100 mg/L. Cultures were incubated at 20°C. Initial biodegradation rates in the 100 mg/L cultures were slower than in the 10 mg/L cultures, indicating substrate inhibition. The initial pH in the culture medium was approximately 7.3. However, pH declined to between 5 and 6 as 2,4-D was utilized.

Breakdown of unacclimated cultures occurred more slowly, exhibiting a lag time of approximately 5-7 days (Kim and Maier 1986). Nearly 90 percent removal of 2,4-D was achieved in about 16 days.

Studies have also shown that the breakdown of 2,4-D occurs more slowly if the appropriate microorganisms are not present. Aly and Faust (1964) reported that 2,4-D concentrations in lighted, aerobic laboratory flasks containing 3 ppm 2,4-D in lake water remained unchanged after 120 days. Schwartz (1967) found that at least 60 percent of the 2,4-D applied to samples of polluted water remained after a period of 3-6 months.

In laboratory culture studies using a *Pseudomonas* bacteria isolated from peat, 2,4-D degradation rates were reported to be affected by the initial cell density, 2,4-D concentration, and Ph (Greer et al. 1990). The lag phase was considerably longer (approximately 80 hours) in the cultures with the lowest initial cell density  $(1.5 \times 10^4 \text{ cells/mL})$ . At higher initial cell densities, the lag phase was reduced to less than 10

hours. The 2,4-D concentration affected the initial lag time, which increased linearly from about 15 hours for the 1 mM 2,4-D concentration (approximately 221 mg/L) to 60 hours for the 13 mM (approximately 2,900 mg/L) 2,4-D concentration. The results also showed that 2,4-D degradation was optimal within a pH range of 4.4 to 7.4. No degradation occurred at the upper (8.1) and lower (3.3) pH values that were tested.

# **Degradation Products**

The following metabolites of 2,4-D produced by Arthrobacter, an indigenous bacteria isolated from native soil, have been identified by Loos (1975) and Tiedje et al. (1969):

- 2,4-Dichlorophenol
- 3,5-Dichlorocatechol
- 2,4-Dichloromuconic acid
- 2-Chlor-4-carboxymethylene-but-2-enolide
- Chloromamaleyacetic acid
- Succinate.

The pathway for metabolism of 2,4-D is shown in Figure 3 (Chakrabarty 1982).

In laboratory culture studies using the *Azotobacter chrococcoum* bacteria isolated from forest soils with 2,4-D as the sole carbon source, Balajee and Mahadevan (1990) identified the metabolites of 2,4-D degradation as 4-chlorophenoxy acetic acid, 4-chlorophenol, 4-chlorocatechol, and 3-chloromuconic acid. Maximum bacterial growth was reported at 10 mM 2,4-D concentration (approximately 2,000 mg/L). Growth was inhibited by 2,4-D concentrations ranging from 20-30 mM (4,400-6,600 mg/L). No growth occurred at the 40 mM concentration (8,800 mg/L).

Recently, Smith and Aubin (1991) studied the metabolites of 2,4-D biodegradation by indigenous bacteria in 4 soils from Saskatchewan (2 clays from Indian Head, 1 clay from Regina, and a sandy loam from White City) that had been treated with 2,4-D within the previous 1 to 5 years. Samples moistened to 85 percent of field capacity were treated with 2 mg/kg 2,4-D (<sup>14</sup>C-labeled and unlabeled) and incubated in the dark at 28°C for 21 days. In all soil samples, there was a rapid initial loss of <sup>14</sup>C labeled 2,4-D which was accompanied by the formation of carbon dioxide, 2,4-dichlorophenol, and

Figure 3 goes here

2,4-dichloroanisole. Recovery of <sup>14</sup>C during these experiments ranged from 86-106 percent. Low recovery was attributed to volatilization (Smith and Aubin 1991).

#### Environmental Half-Lives

Soil and Sediment. Half-lives of 2,4-D (acid) in soil reportedly range from 1.5 to 8.5 days with 90 percent degradation occurring in 5.9 to 25 days (McCall et al. 1981). However, laboratory studies indicate that in newly contaminated soil, an acclimation period or lag time exists before degradation begins, during which time the indigenous bacteria adapt to the presence of 2,4-D. This lag time can last from a few days to a few weeks (W. Chase personal communication 1985).

Kuwatsuka and Miwa (1989) documented a lag of about 10 days prior to the onset of degradation in clay soils treated with 2,4-D. Tests were conducted on two soil samples (a mineral soil containing 26.7 percent kaolin and a volcanic ash containing 37.2 percent clay) collected from a paddy field at an agricultural experiment station in Japan. (Note: The journal article did not specify whether these soils had received prior treatments with 2,4-D.) The growth of 2,4-D-degrading bacteria and degradation rates of 2,4-D in these two soils was evaluated under upland and flooded conditions at a 2,4-D concentration of 25 mg/kg. Moisture content in the upland tests was maintained at 50 percent of the maximum water holding capacity. For flooded conditions, soils were submerged beneath 2 cm of water.

Soil half-lives of approximately 20-50 days were observed. Degradation of 2,4-D was more rapid in the mineral soil under both moisture conditions than the volcanic ash. In both soils, 2,4-D was degraded more rapidly under upland conditions. This difference was more pronounced in the volcanic soil with the half-life decreasing from 50 days under flooded conditions to about 25 days under upland conditions (Kuwatsuka and Miwa 1989).

Studies have shown that biotransformation of 2,4-D can be rapid during repeated exposure of soil to 2,4-D. As described earlier, Smith and Aubin (1991) studied the degradation of 2,4-D in 4 soils that had been treated with 2,4-D in the previous 1-5 years. In laboratory studies using the 4 soils amended with 2,4-D, degradation of the herbicide followed first-order reaction kinetics, with half-lives of 1 and 3 days, respectively, in the clay soils from the two Indian Head sites, and 7 and 9 days,

respectively from the White City sandy loam, and the Regina clay. The loss of <sup>14</sup>C-2,4-D was significantly slower in White City and Regina soils which had not received 2,4-D applications within the previous 5 years (Smith and Aubin 1991).

Smith (1989) described the effects of soil moisture and temperature on the half-life of <sup>14</sup>C-labeled 2,4-D in a heavy clay soil. All soil moisture experiments were conducted at 20°C. At soil moisture contents of 65-100 percent of field capacity the 2,4-D degradation rate was fairly constant (5-10 day half-lives). However, at 50 percent field capacity the half-life increased to 45 days. Temperature experiments were conducted at 85 percent field capacity. The results indicate that the half-lives remained fairly constant (5-10 days) at soil temperatures of 10-25°C. Below 10°C, the half-life increased to about 25 days.

The effects of long term exposure of agricultural soils to 2,4-D were investigated by Smith et al. (1989). The study was conducted over a 35 year period beginning in 1947 at the Indian Head experimental farm in Saskatchewan, Canada. Test plots composed of Indian Head clay were treated each spring with a high and low rate of herbicide. Initially, the tests were conducted using amine, ester, and sodium salt formulations of 2,4-D at rates of 0.56 kg/ha (0.50 lb/acre) and 1.68 kg/ha (1.5 lb/acre). The low rate was reduced to 0.28 kg/ha (0.28 lb/acre) in 1951 and in 1953, the sodium salt was replaced by MCPA. In 1966, the 2,4-D formulations were changed to 2,4-D DMA and isooctyl ester. After 1968, the annual low and high rates of application for all herbicide were changed to 0.42 kg/ha (0.37 lb/acre) and 1.12 kg/ha (1.0 lb/acre), respectively.

Soil samples from each test plot were collected in 1987 from depths of 0-6 inches and 6-12 inches and analyzed for 2,4-D. No residues were detected in any samples at a detection limit of 0.02 mg/kg indicating that the applied 2,4-D was effectively degraded in the soil. The absence of 2,4-D in the deeper (6-12 inch) soil samples also indicates that leaching did not occur.

Laboratory studies were also performed to evaluate the degradation rate of 2,4-D applied to the soils from the previously treated test plots (Smith et al. 1989). Soil samples from the test plots that had received 2,4-D amine and ester applications for 40 years were moistened to 85 percent of field capacity, treated with 2.0 mg/kg of <sup>14</sup>C 2,4-D, and incubated at 20°C for 1 week. Less than 20 percent of the applied 2,4-D remained in all of the previously treated soil samples compared with 55 percent in the control sample.

However, by the eighth day, degradation of 2,4-D in the control was comparable to the pretreated soils with less than 10 percent of the applied 2,4-D remaining in all samples which suggests that microorganisms adapted fairly rapidly to breakdown the 2,4-D.

Studies have shown that the breakdown of 2,4-D in soil is not affected by the presence of other commonly used herbicides such as benzoylprop-ethyl, dicamba, diclofopmethyl, dichlorprop, difenzoquat, dinitramine, flamprop-methyl, nitrofen, picloram, TCA, 2,4,5-T, triallate, and trifluralin (Smith 1979 and 1980). In laboratory investigations, 2,4-D can persist in soils for prolonged periods in the presence of the insecticides carbaryl and parathion, and the herbicide dinoseb (Smith 1989). This phenomena may be caused by a reduction in microbial populations due to the presence of the insecticides. Conversely, microbes may survive, but preferentially degrade compounds other than 2,4-D. However, Smith (1989) concluded that the presence of other pesticides should have minimal effects on 2,4-D degradation under field conditions.

The use of dinoseb is no longer permitted for use in Washington state. The use of parathion and/or carabaryl is restricted, thereby limiting potential interaction between 2,4-D and these compounds. Dinoseb has been banned since 1986 (Schoen-Nesser personal communication 1992). Parathion, which in the past was commonly used in Washington, has been restricted since February 1991 to use on eight cereal crops of which four are grown in Washington (i.e., corn, barley, wheat, and alfalfa). Only carbaryl is used extensively in the state. In addition, neither carbaryl, an organochlorine, or parathion, an organophosphate, are thought to persist long in the environment (Schoen-Nesser personal communication 1992).

#### Water

Half-lives for 2,4-D BEE in water reportedly range from 0.11 to 2.3 days (Reinert and Rodgers 1987). Paris et al. (1981) observed an average half-life of 0.11 days in laboratory studies compared to the 0.3-0.35 days observed in field tank trials (Dodson and Mayfield 1979), and 2.2-2.3 days in lake and reservoir field studies (Oklahoma Water Research 1975; Frank and Comes 1967).

Aqueous half-lives for 2,4-D DMA reportedly range from 3.9 to 11 days (Reinert and Rodgers 1987). Based on the results of jar studies using river water, Robson (1968) estimated the half-life for a 2,4-D amine salt at 3.9 days. In field studies using plastic

pools treated with 2,4-D DMA, the aqueous half-life ranged from 10-11 days (Schultz 1973). Similar results have been reported in lake and reservoir field application studies. For example, a half-life of 6.6 days was estimated in a Fort Cobb Reservoir cove treated with 2,4-D DMA (Reinert and Rodgers 1987), while half-lives of 2.5-6.2 days were reported in Banks Lake (Washington) (Otto et al. 1983). Factors affecting half-life include temperature, pH, oxygen content of the water, and whether or not sufficient populations of 2,4-D degrading microorganisms are present.

Chen and Alexander (1989) in tests conducted on water collected from Beebe Lake in Ithaca, New York found that an acclimation period of approximately 18 days was required before biodegradation of 2,4-D acid occurred. Various tests were conducted using lake water amended with 5 mg/L 2,4-D to evaluate the effects of enzyme induction, potential toxic effects from other contaminants present in the lake samples, and inhibition of bacterial growth due to the presence of protozoa. The results suggest that the acclimation phase represents the time required for bacterial population to increase to the point where chemical loss is detectable. Enzyme induction was found to account for only about 16 hours of the lag period. The presence of protozoa that graze on the bacteria did not appreciably affect the acclimation period.

#### **Sediment**

DeLaune and Salinas (1985) reported that 2,4-D residues in sediment degraded approximately 6 times faster under aerobic conditions when compared to anaerobic conditions. The degradation rate in sediments under aerobic conditions was about 0.012 mg/g-day in Lakes Palourde and Verret in Louisiana compared to only 0.002 mg/g-day under anaerobic conditions.

# Chemical Impurities

Chemical impurities may be introduced into the various 2,4-D formulations during manufacture. The primary impurities found in 2,4-D products include 2,4-dichlorophenol, halogenated dibenzo-p-dioxins (HDD), halogenated dibenzo-furans (HDF), N-nitrosamines, and bis(2,4-dichlorophenoxy) methane (U.S. EPA 1988a; U.S. Forest Service 1988; and IARC 1982). Chemical manufacturers are generally required to report impurities that exceed 1 percent of the 2,4-D product (J. Coombs personal

communication). However, for dioxins, manufacturers are required to report impurities greater than or equal to 0.1 percent (J. Coombs personal communication 1992).

A chemical intermediate, 2,4-dichlorophenol (U.S.F.S. 1988) has been measured in very low concentrations in 2,4-D by eight U.S. manufacturers. Although the most contaminated sample contained approximately 0.3 percent total chlorophenols (which include 2,4-dichlorophenol as well as 2,6-dichlorophenol, 2-chlor- and 4-chlorophenols), chlorophenols were undetected in many of the samples analyzed. Birmingham and Colman (1985) found approximately 0.5 percent 2,4-dichlorophenol contamination in samples of the 2,4-D butoxyethyl ester Aquakleen®) used for a field study of 2,4-D applied to artificial ponds. 2,4-Dichlorophenol is highly volatile and would rapidly dissipate during application if present in 2,4-D. 2,4-Dichlorophenol is also a metabolic by-product of 2,4-D as will be explained later in this report. Mono- and dichlorophenols are reportedly toxic to fish (Hattula et al. 1981; Holcombe et al. 1980). However, there is presently no requirement to eliminate 2,4-dichlorophenol from 2,4-D formulations.

Because HDD and HDF are structurally similar to 2,4-D and could be generated under certain manufacturing and process conditions, EPA has required manufacturers to analyze their 2,4-D products for these potential impurities (U.S. EPA 1988a). Some of the polyhalogenated dibenzo-p-dioxins and dibenzofurans are mutagenic, oncogenic, teratogenic, and cause reproductive toxicity. Required detection limits for dioxins range from 0.1 to 1,000 ppb, depending on the isomer; 2,4,7,8-TCDD has the lowest required detection limit (J. Coombs personal communication 1992). Due to the high cancer potency of dioxins, exposure to dioxins at levels below the 0.1 ppb detection limit could result in cancer risks to humans. However, the extent to which dioxins have been detected in 2,4-D was unable to be ascertained for this report, because this information is considered by EPA to be confidential (J. Coombs personal communication 1992).

2,7-Dichlorodibenzo-p-dioxin (DCDD) was found in 3 of 30 samples of 2,4-D manufactured in the U.S (U.S.F.S. 1988). Concentrations in the positive samples ranged from 25-60 ug/L. DCDD is a suspected teratogen and carcinogen, but is a million times less toxic than 2,3,7,8 TCDD dioxin.

N-nitrosodiphenylamine was detected at 300 ug/L in a 2,4-D dimethylamine salt that was stored in metal containers which had been presprayed with sodium nitrate as an anti-oxidant (IARC 1982).

Huston (1972) identified bis(2,4-dichlorophenoxy)methane as the major contaminant in 2,4-D. Other minor contaminants that were identified include bis(2,6-dichlorophenoxy)methane and 2,2',4,6'-tetrachlorodiphenoxymethane.

#### Plant Accumulation

Many agricultural crops including grapes, cotton, and tomatoes are sensitive to 2,4-D. Stanford Research Institute conducted a greenhouse experiment to determine the effects of 2,4-D applied in irrigation water on potatoes, grain sorghum, soybeans, carrots, Romaine lettuce, and onions (Gangstad 1986). 2,4-D DMA was applied at two growth stages to each crop. Although application rates were greater than those typically used for weed control, residues in all crops evaluated were below FDA tolerances for food crops. The highest residues (0.11-0.33 mg/kg) were reported in Romaine lettuce.

Two applications of 2,4-D (0.1, 0.5, and 2.5 lb/acre (0.11, 0.56, and 2.80 kg/ha) in 2 acre-inches of water by furrow irrigation; and 0.01, 0.1, and 1.0 lb/acre (0.011, 0.11, and 1.1 kg/ha) in 2 acres-inches of water by sprinkler irrigation) were applied to sugar beets, sweet corn, and soybeans to evaluate the effects on plant growth and uptake of 2,4-D (Gangstad 1986). Although some minor abnormalities in plant growth were observed (e.g., abnormal curvature of petioles, wilting and slumping, and some chlorosis or necrosis in sugar beets; leaf chlorosis in soybeans; and desiccation of the lower leaves of sweet corn), no reduction in plant yields occurred when the herbicide was applied via furrow irrigation. After 7 days, 2,4-D residues were detected in all plants at the two higher treatment rates in concentrations ranging from 0.009-1.10 mg/kg (wet weight). However, 2,4-D was not detected in the edible portions of the plants at the time of harvest. No 2,4-D was detected at the lower treatment rate.

No reduction of crop yields was observed when 2,4-D was applied via sprinkler irrigation. Although temporary drooping and wilting was reported in sugar beets, the fresh weight and root yields were increased. In soybeans, growth was temporarily suppressed and some early chlorosis was observed, but seed yields and quality were not affected. No visible injury was observed to dwarf corn as a result of the treatment. 2,4-D residues were typically detected in the plant roots and foliage (0.008-3.8 mg/kg) 2 days after treatment, but no residues were found in the edible portions of the plants at harvest time (Gangstad 1986).

# 2.3.2 Transport Mechanisms

This section discusses the potential transport of 2,4-D via groundwater, surface water, and air. Leaching of herbicide applied to upland soils could potentially contaminate groundwater. Surface water contamination may occur either through direct application of 2,4-D for aquatic weed control, wind drift from adjacent upland treated areas, or via surface water runoff that comes in contact with treated upland areas. This section addresses the potential for contamination via surface runoff and wind drift.

#### Groundwater

As explained earlier, the 2,4-D ester and salt formulations are converted fairly rapidly to the parent acid compound. Existing information on the chemical characteristics of 2,4-D acid suggest that it would be susceptible to leaching. For example, the acid is fairly soluble in water (300-9000 mg/L) and is not strongly sorbed to soil particles (K<sub>d</sub> values are less than 5 for most soils). However, 2,4-D has not typically been found to contaminate groundwater, apparently due to degradation by soil microorganisms. 2,4-D has been detected in approximately 100 out of over 1,700 groundwater samples collected from 9 states in the U.S. (Dynamac 1988). Most of the contamination problems were associated with point sources (i.e., spills, illegal dumping). The highest reported concentration (36.5 ug/L in a well in Idaho) was believed to have been caused by a point source. The highest reported groundwater concentration of 2,4-D that could be attributed to nonpoint sources (i.e., leaching caused by normal use) was 4.2 ug/L.

2,4-D has also been detected in only a small number of drinking water supplies sampled as part of national and region surveys. Reported contamination levels have generally been below 0.5 ug/L, with most less than 0.1 ug/L (U.S. EPA 1987). Contamination has been reported more often in surface waters than ground water, although no exceedances of the recommended maximum contaminant level for drinking water (100 mg/L) have been reported.

#### Surface Water

Little information is available to evaluate offsite transport of 2,4-D in surface water runoff from upland treated areas. However, given its relatively high solubility in water, the potential does exist for surface runoff to contain 2,4-D residuals. Meru et al. (1990)

studied the offsite transport of 2,4-D applied to power line rights-of-way and concluded that less than 0.1 percent of the applied 2,4-D was transported offsite in stormwater runoff.

The tests were conducted on two power line rights-of-way in Ontario, Canada. A mixture containing picloram (4-amino-3,5,6-trichloropicolinic acid) and 2,4-D both formulated as tri-isopropanolamine salts was applied on two occasions at rates of approximately 7.2 lb/acre picloram and 29 lb/acre 2,4-D to sandy loam and sandy clay loam soils located on slopes of 16-19 percent. Runoff samples were collected 0.14, 0.57, 1, 2, 4, 8, 11, 15, and 48 weeks after application from collection trenches located 10, 33, and 98 feet downslope of the treated area. 2,4-D residuals were detected in 11 of 57 water samples analyzed at concentrations of 0.1-0.5 ug/L. Residuals were detected only in the two closest trenches. No 2,4-D residual was detected in the water collected from the trench 98 feet away from the treated area (Meru et al. 1990).

#### <u>Air</u>

Air transport of 2,4-D during application may occur due to volatilization of the herbicide as well as through wind drift and spray losses. All of the 2,4-D formulations registered for aquatic use are characterized as low to nonvolatile. Therefore, the potential for offsite impacts from herbicide vapors is relatively low. However, label information for ester formulations typically state that at high temperatures (i.e., >95°F) vapors from normal applications may injure susceptible plants.

The Washington Department of Agriculture currently permits only the low volatile ester formulations of 2,4-D to be used on agricultural crops (H. Moia personal communication 1992). Low volatile esters are defined as those containing 6 or more carbon molecules in the ester chain. The ester formulations registered for aquatic use (i.e., butoxyethanol ester and isooctyl esters) are classified as low volatile esters.

Wind drift and spray losses represent the primary air transport pathway for 2,4-D. Labelling instructions typically provide the following recommendations to reduce wind drift: (These are manufacturers recommendations and may be requirements of some state agencies)

- Use nozzle pressure of 20 psi or less
- Use nozzles that produce a coarse spray pattern
- Apply herbicide only when wind velocity is less than 5 miles per hour
- Spray only when there is no potential for a temperature inversion.

Breeze and Rensburg (1991) determined that vapor of the free acid of 2,4-D is toxic to tomato and lettuce plants. In greenhouse experiments, tomato and lettuce plants were exposed to vapor containing 0.001-0.6 ug/L [\frac{14}{C}-phenyl]2,4-D for periods of 6-72 hours. Forty days after exposure, the lettuce plants exposed to the highest dose (0.6 ug/L) showed slight symptoms (stem elongation and twisting of veins in the larger leaves). Tomato plants exhibited more severe effects ranging from leaflets on leaves exposed to 0.6 ug/L for 6 hrs to malformed leaves and thinning of the stems on plants exposed to 0.6 ug/L for 72 hours. Reductions in shoot dry weight of 10-20 percent were also reported.

In the study of herbicide movement from power line rights-of-way described earlier, downslope drift of herbicide was detected even though spray crews avoided spraying when there was a noticeable wind (Meru et al. 1990). Trace residues of 0.1-0.5 mg/m<sup>2</sup> of 2,4-D were detected in petri dishes located as far as 33 feet downslope from the treatment area.

#### 2.3.3 Summary of Field Tests

This section summarizes the results of field studies concerning the persistence of 2,4-D in the aquatic environmental when directly applied for the control of aquatic weeds. Studies have been conducted on a number of water bodies ranging from large reservoirs in the southeast to canals and lakes in the northwest. The range of conditions observed in these studies should be representative of conditions that would be encountered in water bodies in Washington state.

Studies using 2,4-D BEE (Aquakleen®) in Skaha Lake and Okanagan Lake (British Columbia) indicate that 2,4-D concentrations in the water rapidly dissipate after treatment, declining to below the analytical detection limit within 0-22 days (Dynamac 1988). The estimated half-life in water was less than 3 days. Treatment rates during the studies varied between 11 and 45 kg/ha (9.8 and 40 lb/acre). The concentrations in lake water reached 0.033-3.25 mg/L within 0-11 days after treatment for the 40 lb/acre

treatment, compared with 0.067 mg/L for the 33 kg/ha (29 lb/acre treatment), and 0.099-0.36 mg/L for the 22 kg/ha (20 lb/acre) treatment. The highest concentrations measured in water samples collected nearly 800 feet from the treatment site was 0.017-0.131 mg/L.

By comparison, the highest reported concentrations in the lake sediments (7.15-288 mg/kg) occurred 8-161 days after treatment for the 45 kg/ha (40 lb/acre) treatment, 57.3 mg/kg at 52 days for the 33 kg/ha (29 lb/acre) treatment, and 12.7-17.6 mg/kg at 37-49 days for the 22 kg/ha (20 lb/acre treatment).

At one site in Okanagan Lake, treated with 11, 23, and 33 kg/ha (10, 20.5, and 29.4 lb/acre) 2,4-D BEE, the concentration of 2,4-D in the water reached a maximum of 4,000 mg/L 6 days after treatment, but was not detected after 59 days. Sediment concentrations at this site reached a high of 34 mg/kg 2 days after treatment and were undetected after 86 days (Dynamac 1988).

In an irrigation canal treated with 0.43 lb of 2,4-D DMA, 2,4-D was detected in the water as far as 6 miles downstream of the treatment site within about 1 hour of application (Dynamac 1988). Maximum concentrations in samples collected 1, 3, and 6 miles downstream of the site were 84-143 ug/L, 103-110 ug/L, and 54-61 ug/L, respectively. The 2,4-D half-lives at the three sites ranged from <16 minutes at the 1 mile site to 13-133 minutes at the 6 mile site.

Hoeppel and Westerdahl (1983) monitored the dissipation of 2,4-D DMA and BEE residuals in Lake Seminole, Georgia after 27 acre test plots were treated to control Eurasian water milfoil. Average water depth in the plots ranged from about 3-6 feet. Two plots were treated with 22.5 and 45 kg acid equivalent (a.e.) per ha (20 and 40 lb/acre) of 2,4-D DMA (Weedar 64®) herbicide and two were treated with 22.5 and 45 kg a.e. per ha (20 and 40 lb/acre) of 2,4-D BEE (granular Aquakleen®) in June 1981 via aerial spray. Water temperatures during the study varied from 29.6-30.3oC.

The 2,4-D BEE rapidly hydrolyzed to 2,4-D acid, with less than 0.01 mg/L present in water in the ester form. The degradation product 2,4-dichlorophenol was also present at less than 0.01 mg/L. 2,4-DMA rapidly dissociated to 2,4-D acid and dimethylamine. The potentially toxic transformation product, dimethylnitrosamine was detected at concentrations below 0.01 mg/L.

The concentration of 2,4-D in water in the 45 kg/ha 2,4-D DMA plot reached 3.6 mg/L on the day after application. The highest concentration in the 22.5 kg/ha plot (1.3 mg/L) was also observed one day after treatment. 2,4-D concentrations declined to <0.01 mg/L within 7 days. In the 2,4-D BEE plots, the highest concentration (0.68 mg/L) was observed one day after treatment on the plot treated with 45 kg/ha 2,4-D BEE. Similar one-day concentrations (0.51-0.65 mg/L) were also observed in the 22.5 kg/ha plot which was located in shallower water. 2,4-D concentrations declined to <0.01 mg/L by day 13 at both plots.

Interpretation of the sediment residue analyses were complicated by analytical quality assurance/quality control problems [i.e., low recoveries of 2,4-D (28 percent), 2,4-dichlorophenol (31 percent), and dimethylnitrosamine (48 percent) in spiked samples]. However, the report concluded that little accumulation of 2,4-D occurred in the sediments. The maximum sediment concentration reported during the study (8.0 mg/kg 2,4-D) occurred 7 days after treatment in the low rate 2,4-D BEE plot. The highest 2,4-dichlorophenol concentration (5.6 mg/kg) was observed on the high rate 2,4-D BEE plot.

Fish samples (large mouth bass, sunfish, bluegill, catfish, and gizzard shad) were collected up to 69 days post-treatment. None of the fish from the two 2,4-D DMA (Weedar 64®) plots contained detectable concentrations (0.1 mg a.e./kg) of 2,4-D in muscle tissue. However, 2,4-D was detected in 18 of the 20 gizzard shad and 4 of 24 game fish collected from the 2,4-D BEE treatment plots through day 13. The highest concentration in the muscle tissue of the shad (3.85 mg/kg) was observed on day 1, declining to 1 mg/kg by day 28. In game fish, the highest muscle tissue concentration (5.1 mg/kg) was observed 4 days after treatment, declining to 0.1 mg/kg by day 13 (Hoeppel and Westerdahl 1983).

Birmingham and Colman (1985) applied 2,4-D BEE crystals (Aquakleen®) at a rate of 23 kg/ha (20.5 lb/acre) to artificial ponds planted with Eurasian watermilfoil. Analysis of the Aquakleen® crystals indicated that the active ingredient contained 0.5 percent 2,4-dichlorophenol. The ponds were approximately 3 feet deep and were lined with about 6 inches of virgin loam soil. Water, sediment, and plant material samples were collected 1 day after treatment and at periodic intervals for 180 days. Water temperature in the ponds dropped from 25°C at the time of treatment to below freezing within 60 days of treatment.

Results are summarized in Table 6. A mass balance on total 2,4-D residues indicates that the largest proportion of the applied herbicide was present in the water column throughout the study. 2,4-D BEE concentrations in water decreased from a high of 0.16 mg/L the first day after application to 1 ug/L within 15 days. The 2,4-D acid level in the pond reached a maximum concentration of 3.0 mg/L about 15 days after treatment, gradually declining to 1 mg/L after 85 days. Degradation by-products such as 2,4-dichlorophenol (2,4-DP) and 2,4-dichloroanisole (2,4-DCA) were not detected at detection limits of 0.01 mg/L at any time during the study.

2,4-D residues in pond sediments persisted for longer periods of time. The maximum 2,4-D BEE concentration (1.7 mg/kg) occurred in the sediment about 7 days after treatment, and then rapidly declined to <0.1 mg/kg over the next 42 days. 2,4-D acid residues declined from an initial high of 6.7 mg/kg after 1 day to about 0.5 mg/kg after 7 days.

Residues of 2,4-D were also detected in the milfoil. Plant uptake was highest (206 mg/kg) 9 days after treatment and then declined to <20 mg/kg (Birmingham and Colman 1985).

Schultz and Gangstad (1990) described the results of 2,4-D treatment using the dimethylamine salt formulation (Weedar 64®) in ponds located in Georgia (3 golf course ponds) and Florida (4 private ponds) to control water hyacinth. The ponds were treated with a one time application of 2.24, 4.48, and 8.96 kg/ha (2, 4, and 8 lb/acre) in July, 1971. Samples of water, sediment, and fish were collected periodically for 140 days after treatment and analyzed for 2,4-D residues.

2,4-D residues in water in the Florida ponds were highest (0.345 mg/L) 3 days after treatment in the pond treated with 8 lb/acre 2,4-D DMA, decreasing to 0.025 mg/L by day 7, and to 0.005 mg/L within 14 days. At the lowest treatment rate (2 lb/acre) 2,4-D concentrations declined to 0.005 mg/L within 3 days after treatment. In the pond treated with 4 lb/acre 2,4-D DMA, the highest concentration (0.172 mg/L) occurred 3 days after treatment, declining to 0.048 mg/L by day 7, and to 0.005 mg/L by day 14.

In the Georgia ponds, the highest 2,4-D concentration in water samples collected from the pond treated with 3 lb/acre 2,4-D DMA (0.692 mg/L) occurred 3 days after treatment, declining to 0.395 mg/L by day 7, and to less than 0.005 mg/L after 28 days.

**Table 6.** Concentration of 2,4-D residues in pond components.

Days after	2,4-D Con	centration (n	ng/kg)	Concentration	on Factor
application	Plant	Mud	Water	Plant/Water	Mud/Water
1	136	8.0	1.8	75.5	4.4
. 7	206	4.4	2.2	93.6	2
13	98	4.3	3.0	32.7	1.4
34	16	1.6	1.6	10	1
55	16	1.0	1.3	12.3	0.8
82	8	0.4	1.1	7.3	0.4
111	a	0.5	0.8	NA	0.6
182	NA	0.6	0.2	NA	3

NA = No data available.

Reference: Birmingham and Colman (1985)

<sup>(</sup>a) Ponds contained about 4,000 kg water and 290 kg mud, and from day 1 to day 20, and day 27 onward, contained 0.5 kg plant material, respectively.

In comparison, at the other application rates used in the test, the highest residuals occurred 3 days after treatment (0.087 mg/L with 2 lb/acre treatment and 0.390 mg/L with 4 lb/acre treatment) and declined to 0.005 mg/L 28 days after treatment.

The highest 2,4-D concentration (0.046 mg/kg) was observed 3 days after treatment with 8 lb/acre 2,4-D DMA in the Florida pond sediments, declining to 0.008 mg/kg by day 7 and 0,005 mg/kg by day 14. In the Georgia ponds, the greatest concentration (0.042 mg/kg) was observed 7 days after treatment. However, residues declined to 0.013 mg/kg by day 14 and 0.005 mg/kg by day 28.

Fish were kept in live cages in the Florida ponds for up to 3 days after treatment. The highest residues (0.005-0.080 mg/kg) occurred 1 day after treatment. There were no detectable residues of 2,4-D in any fish caught 3 and 7 days after treatment. However, 14 days after treatment, one fish contained detectable residues of 2,4-D which was believed to have been caused by the release of 2,4-D from decaying vegetation. In the Georgia ponds, the highest residue of 2,4-D (0.075 mg/kg) was observed in one of three bluegills collected 14 days after the pond was treated with 8 lb/Ac. No residues of 2,4-D were detected in fish caught from the Georgia ponds 3 and 7 days after treatment.

Morris and Jarman (1981) observed a significant increase in total phosphorus concentrations in Kerr Lake, Oklahoma after treatment with 2,4-D BEE to control Eurasian watermilfoil. Eight areas in the lake totalling 463.3 ha (1145 acres) were treated with 4,218 kg (9,300 lbs) of granular Aquakleen® herbicide in June, 1978. One of the test areas (202.6 ha; 501 acres) received a second herbicide application in August (3,833 kg; 8,450 lbs). Water samples collected at 10 stations (8 treatment areas plus 2 controls) before and after treatment were analyzed for total phosphorus, ammonia, 2,4-D, and 2,4-dichlorophenol.

2,4-D was detected at 3 ug/L in only 1 sample collected within 4 hours of treatment. The breakdown product, 2,4-dichlorophenol was never detected. The total phosphorus concentration was significantly higher at three of the eight application sites after treatment. The highest concentration observed during the study was 0.3 mg/L. A significant decrease in ammonia concentration was also observed at one station (Morris and Jarman 1981).

# 2.3.4 Summary of 2,4-D Environmental Fate

Breakdown of 2,4-D in the receiving environment occurs primarily through biodegradation, although photolysis by ultraviolet light may also be a significant factor in clear, shallow water. The various salt and ester formulations of 2,4-D that are registered for aquatic use in Washington state are rapidly converted to the parent acid compound, which is biodegradable, via hydrolysis and dissociation reactions.

Half-lives of 2,4-D in water are quite variable, ranging from a few days to several months. Microbial degradation generally occurs more rapidly at higher temperatures and under aerobic conditions. In addition, studies have shown that an initial lag period, during which time little biodegradation occurs, as microorganisms acclimate to 2,4-D and achieve a sufficient population for measurable degradation to occur. In studies with unacclimated laboratory cultures, Kim and Maier (1980) measured a 5-7 day lag period and also observed inhibition at concentrations of approximately 100 mg/L 2,4-D.

Half-lives of 2,4-D in agricultural soil typically range from about 1.5-8.5 days, although half-lives as long as 25 days have been reported (McCall et al. 1981; Kuwatsuka and Miwa 1989). Repeated exposure results in shorter half-lives as microorganisms become acclimated to 2,4-D. Factors affecting soil half-life include temperature, soil moisture content, organic matter content, and soil pH.

Smith et al. (1989) also showed that long-term application of 2,4-D to agricultural soils did not cause significant accumulation or leaching of 2,4-D in the soil profile. The study was conducted over a 35-year period, during which time test plots were treated annually with 0.28-1.68 kg/ha (0.25-1.5 lb/acre) 2,4-D (applied as amine and ester formulations). Low accumulation and leaching was attributed to effective degradation by soil microorganisms.

2,4-D residues have been shown to persist for longer periods in aquatic sediments, presumably due to less rapid biodegradation resulting from the lower oxygen content and lower temperatures associated with aquatic sediments. Half-lives of approximately 20-50 days have been reported in clay soils under flooded conditions (Kuwasuka and Miwa 1989). In aquatic field studies, 2,4-D BEE residues in lake sediments of up to 140 ug/kg have persisted for as long as 300 days after the initial application (Dynamac 1988). The majority of the field studies completed to date indicate that the maximum concentration of 2,4-D in sediments occurs within 3-6 days after treatment declining to below analytical

detection limits within approximately 14-161 days (Dynamac 1988; Schultz and Gangstad 1990).

Chemical impurities and metabolic byproducts may also be present in the original formulation or generated during the degradation of 2,4-D in the receiving environment. 2,4-Dichlorophenol is the primary metabolite of 2,4-D microbial degradation. Mono- and chlorophenols are reportedly toxic to fish. Other metabolites that have been detected in laboratory studies include 4-chlorophenoxy acetic acid, 4-chlorophenol, 4-chlorocatechol, 3-chloromuconic acid, 3,5-dichlorocatechol, 2,4-dichloromuconic acid, 2-chlor-4-carboxymethylene-but-2-enolide, chloromamaley- acetic acid, and succinate.

Chemical impurities that have been reported in 2,4-D formulations include 2,4-dichlorophenol, halogenated dibenzo-p-dioxins, halogenated dibenzofurans, N-nitrosamines, and bis(2,4-dichlorophenoxy)methane. 2,4-Dichlorophenol, a chemical intermediate has been detected in 2,4-D products manufactured in the U.S. Concentrations are typically very low, however, a maximum concentration of 0.5 percent 2,4-dichlorphenol was reported in a 2,4-D BEE formulation (Birmingham and Colman 1985). Some of the polyhalogenated dibenzo-p-dioxins and dibenzofurans have been found to be mutagenic, oncogenic, teratogenic, and to cause reproductive toxicity.

Although 2,4-D is relatively mobile in soil due to its high solubility and low adsorption characteristics, groundwater contamination has not been widely reported (2,4-D detected in about 100 out of over 1700 groundwater samples collected from 9 states in the U.S.). Most cases of groundwater contamination have been associated with point sources, such as spills, with a maximum reported concentration of 36.5 ug/L. The concentrations of 2,4-D in groundwater due to nonpoint source contamination (e.g., leaching due to normal application) have generally been below 0.1 ug/L (Dynamac 1988).

The 2,4-D formulations registered for aquatic use are characterized as low to nonvolatile which reduces the potential for damage to adjacent crops due to volatilization. However, recent data indicate that spray drift can occur even when 2,4-D is applied under calm wind conditions. For example, Meru et al. (1990) detected trace amounts of 2,4-D (0.1-0.5 mg/m²) in petri dishes placed as far as 33 feet downslope of treated power line rights-of-way. In addition, labeling information indicates that at temperatures exceeding 95°F, which are common in eastern Washington during the summer, vapors from normal applications may injure susceptible plants. Because wind drift and spray losses have been

observed during normal application, the use of 2,4-D to control aquatic weeds in areas adjacent to sensitive crops should be avoided.

# 3.0 ADJUVANTS: ENVIRONMENTAL FATE AND EFFECTS

#### 3.1 INTRODUCTION

Adjuvants are chemicals that are added to a pesticide mixture prior to application to enhance the performance of the original pesticide formulation. They encompass a wide variety of products including acidifiers, attractants, buffers, defoaming agents, deposition aids, extenders, spray colorants, spreader-stickers, surfactants, and thickeners that perform one or more of the following functions:

- Improve foliage wetting and coverage
- Reduce evaporation rate of the spray
- Improve weatherability of spray deposit
- Enhance penetration and translocation
- Adjust pH
- Improve compatibility of mixtures.

This report describes the environmental fate and effects of the following three agricultural adjuvants:

- R-11 Spreader Activator
- LI-700 Penetrating Surfactant
- Valent X-77 Spreader.

These three adjuvants are marketed primarily as surface active agents, or surfactants and are usually used only with glyphosate. Their main function is to provide an even coverage of the herbicide on the surface of the plant, although they may also improve herbicide penetration. For aquatic plants, whose foliage often has a waxy surface that resists wetting, surfactants are commonly needed to reduce surface tension and promote wetting.

Of the two herbicides being considered for control of aquatic weeds in Washington state (glyphosate and 2,4-D), surfactant use is required only for glyphosate. Glyphosate functions by disrupting photosynthesis, respiration, and the synthesis of nucleic acids in

plant tissue. It must absorb through the plant foliage (i.e., leaves and stems) to be effective. Studies have shown that 20 to 30 percent of glyphosate applied to leaf vegetation is absorbed within 12 hours of application (Garnett 1991). Therefore, use of surfactants to promote even coverage on plant foliage will improve the effectiveness of glyphosate. In comparison, 2,4-D is usually applied in a petroleum hydrocarbon carrier, such as kerosene, or is applied in granular form (e.g., Aquakleen®). Thickeners such as NalcoTrol® are sometimes used with 2,4-D at a rate of about 0.5 percent to reduce wind drift.

Pesticide adjuvants must be approved by the U.S. Environmental Protection Agency under 40 CFR 180.1001. Because chemical adjuvants are not part of the original pesticide formulation and are not considered active ingredients, they are not subject to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) requirements for pesticide registration (40 CFR 152). As a result, much of the environmental fate and toxicity information available for pesticides is not currently available for many of the adjuvants. Only limited toxicity data are available for the three adjuvants (R-11, LI-700, and X-77) of interest for aquatic weed control in Washington state. This report summarizes compound-specific information that is available from the manufacturers or reported in the scientific literature. Where compound-specific information is unavailable, information regarding other similar adjuvants is presented.

#### 3.1 ENVIRONMENTAL FATE

This section summarizes available information on the chemical characteristics of each of the three adjuvants that affect its environmental persistence and mobility (e.g., solubility and biodegradation).

#### 3.2.1 Chemical Characteristics

<u>R-11 Spreader Activator</u>. R-11, distributed by Wilbur-Ellis Company, contains octylphenoxypoly(ethoxyethanol), isopropyl alcohol, and compounded silicone. It is an alkylphenol ethoxylate nonionic surfactant with the following general chemical formula:

$$CH_3 - (CH_2)_5 - CH - CH_3$$

$$x = 4.30$$
 O - CH<sub>2</sub> - CH<sub>2</sub> - (O - CH<sub>2</sub> - CH<sub>2</sub>)<sub>x</sub> OH

R-11 is a clear liquid with an alcohol-like odor. It is soluble in water and has a specific gravity of 1.0.

<u>LI-700 Penetrating Surfactant</u>. LI-700 is manufactured by Loveland Industries, Inc. It contains a mixture of phosphatidylcholine and methylacetic acid. Phosphatidylcholine, otherwise known as lecithin, is a naturally occurring complex lipid, or phosphoglyceride (Lehninger 1975). Phosphoglycerides are constituents of most plant and animal cell membranes. The phosphatidylcholine molecule contains both positive and negative charges and is referred to as zwitterionic. The chemical formula for phosphatidylcholine is shown below:

# $CH_2(R)CH(R')CH_2OPO(OH)O(CH_2)2N(OH)(CH_3)_3$ where R and R' represent fatty acid groups.

LI-700 is a dark brown liquid with a vinegar-like odor. It is miscible in water and has a specific gravity of 1.0302. Although it is not classified as corrosive, because it contains methylacetic acid, LI-700 is often used as an acidifying agent. LI-700 is incompatible with strong oxidizers.

<u>Valent X-77 Spreader</u>. X-77 spreader activator, distributed by Valent U.S.A. Corporation contains alkylarylpoly(oxyethylene), glycols, free fatty acids, and isopropyl alcohol. Like R-11, X-77 is an alkylphenol ethoxylate nonionic surfactant. It is highly volatile and flammable. Valent U.S.A. Corporation declines to reveal the chemical formulation for X-77. The generic formula for alkyarylpoly(oxyethylene) surfactants is shown below:

$$CH_3 - (CH_2)_n - CH - CH_3$$

$$n = 5.7$$
  
 $x = 4.30$   $O - CH_2 - CH_2 - (O - CH_2 - CH_2)_x OH$ 

# 3.2.2 Solubility

Information concerning the solubility of the adjuvants R-11, LI-700, and X-77 is not available. Because surfactants tend to concentrate at interfaces rather than in the bulk solution, it is likely that when applied in aquatic environments for weed control, the concentration of these adjuvants would be greatest near the water surface. Both R-11 and X-77 are soluble in water (Wilbur-Ellis 1992; Valent 1991). However, LI-700, which is composed primarily of phosphatidylcholine (a zwitterionic surfactant that has an extremely low solubility in water [Tadros 1984], is likely to be less soluble than either R-11 or X-77).

Surfactant molecules are composed of hydrophilic and hydrophobic groups. The presence of the hydrophilic group provides the surfactant's water solubility. In the two nonionic alkylphenol ethoxylate surfactants (R-11 and X-77), the hydrophilic group is composed of polyoxyethylene (CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub> and the hydrophobic group is composed of alkylphenol. Nonionic surfactant solubility generally increases with increasing polyoxyethylene content (Kirk-Othmer 1983).

Because heating reduces the hydration of the hydrophilic portion of the surfactant molecule, solubility of the ethoxylates is inversely related to temperature (Tadros 1984). As dehydration occurs, surfactant molecules aggregate into micelles. The temperature at which micelle formation occurs, as evidenced by an increase in turbidity of the solution, is known as the cloud point. Nonionic surfactants are typically most effective at temperatures between 10°C below and 20°C above the cloud point (Tadros 1984).

The addition of electrolytes such as sodium chloride also reduces the solubility of nonionic surfactants (Meguro et al. 1987), which suggests that these surfactants may be less effective when used in marine environments.

# 3.2.3 Biodegradation

No product-specific biodegradation studies have been conducted using R-11, LI-700, or X-77. Studies using other alkylphenol ethoxylates similar to R-11 and X-77 have shown that with proper acclimation, substantial biodegradation of these surfactants can occur under both field and laboratory conditions (Swisher 1987). However, biodegradation of surfactants with alkylphenol hydrophobes (similar to the R-11 and X-77 adjuvants) containing either linear or branched alkyl groups is generally much more difficult than that of other nonionic surfactants. The degree and rate of biodegradation is influenced by several factors, including the number of ethylene oxide units per mole of surfactant, shape of the alkyl group, location of the benzene ring attachment in the alkyl chain, and temperature (Swisher 1987; Sivak et al. 1980). In general, biodegradation is more rapid for nonionic surfactants with chemical structures that exhibit less branching of the alkyl groups, fewer numbers of ethylene oxide units, and benzene ring attachment to a primary carbon in the alkyl chain (A.D. Little 1977; Swisher 1987).

Studies indicate that biodegradation of nonionic ethoxylate surfactants occurs via three main pathways (Swisher 1987):

- Cleavage of the hydrophilic and hydrophobic units
- Attack at the far end of the hydrophobe, with biodegradation proceeding inward
- Attack at the far end of the ethoxylate chain.

The major degradative pathway appears to be shortening of the ethoxylate chain (Swisher 1987).

The alkylphenol ethoxylates are generally considered to undergo fairly complete primary degradation (i.e., degradation to the extent that the surfactant characteristics are eliminated). However, ultimate degradation, or the complete conversion to carbon dioxide and water, is slow and may not be complete (Swisher 1987). Incomplete breakdown of the ethoxylates results in the generation of chemical intermediates, primarily polyethylene glycol (Swisher 1987). Studies have shown that polyethylene glycol is biodegradable, but breakdown occurs relatively slowly. Because its toxicity is much lower than that of its precursors (Conway et al. 1983), polyethylene glycol does not

appear to be a significant problem in the receiving environment. Additional information on the persistence of polyethylene glycol is needed to assess its environmental impact.

Short ethoxylates have also been identified as potential intermediates (Swisher 1987). Because the aquatic toxicity of these short ethoxylates is relatively high, there is some concern about potential environmental effects. However, insufficient data are available to determine whether the formation of these intermediate by-products represents a problem for aquatic use.

No information concerning the breakdown of phosphatidylcholine surfactants such as LI-700 was found during this review. Because phosphatidylcholine is a naturally occurring lipid, it is likely that this product is subject to biodegradation. The rate and degree of breakdown are unknown.

Data summarized by Swisher (1987) demonstrate that biodegradation rates and effectiveness for the octylphenol ethoxylates vary considerably. Three to 100 percent reductions in surfactant concentration occurring over a period of 1 to 77 days have been reported (Swisher 1987). Most of these studies were conducted under laboratory conditions with higher concentrations of the microorganisms than might typically be present under field conditions. Therefore, it is likely that degradation may occur more slowly in the aquatic environment.

Acclimation can reduce the time for breakdown to occur. Lashen et al. (1967) studied surfactant degradation in water samples from the Schuylkill River (Delaware) and Ohio River using a tertiary octylphenol ethoxylate (t-OPE<sub>10</sub>). In laboratory tests, biodegradation of the surfactant in unacclimated river samples took at least 1 week compared to several days using acclimated samples.

Lashen et al. (1966) studied the breakdown of a tertiary octylphenol ethoxylate (t-OPE<sub>10</sub>) in a continuous-flow activated sludge system. The results indicate that 90 to 100 percent removal of the surfactant was achieved after 10 to 15 days of acclimation with only 65 percent removal of the polyethoxylate chain. No information is available for degradation of the phenolic compounds.

Studies also indicate that microorganisms capable of degrading surfactants may not be ubiquitous. In laboratory tests of an octylphenol ethoxylate (OPE9) in an activated sludge

system using indigenous bacteria, Mann and Reid (1971) report that less than 20 percent of the surfactant was degraded after 46 days of operation. When activated sludge from a municipal wastewater treatment plant was added to the system, biodegradation of the surfactant increased to about 80-90 percent.

Temperature also plays a significant role in biodegradation. Mann and Reid (1971) conducted field trials on a trickling filter system and found that degradation of a tertiary octylphenol ethoxylate increased from a low of 20 percent between March and June to 80 percent between September and October, dropping back to 20 percent in December. In comparison, removal rates for linear primary alcohol ethoxylates were 80-90 percent during the winter months.

Birch (1984) also documented temperature-related changes in bacterial growth rates in a laboratory activated sludge unit. The activated sludge system was operated at temperatures ranging from 6°C to 15°C with sludge retention times of 2 to 10 days. At 15°C and 2 to 10 day retention times, degradation of tertiary octylphenol ethoxylate ranged from about 90 to 95 percent. However, at 6°C and retention times of 2 and 4 days, surfactant removal decreased to 5 percent and 50 percent, respectively. These results indicate that lower growth rates that occurred at the lower temperatures resulted in lower surfactant removal.

#### 3.2.4 Impurities

Because synthesis of pure nonionic surfactants is difficult, most commercial surfactants typically contain a number of impurities (Meguro et al. 1987). Impurities that are commonly present in the alkylphenol ethoxylates include (Tadros 1984):

- Polyethylene glycol (present at concentrations of 0.2 to 3 percent, depending on the molecular weight of the surfactant)
- Aldehydes (present at concentrations of 10 to 30 ppm in ethylene oxide, which is used in the production of ethoxylate surfactants)
- Inorganic catalyst residues (i.e., sodium, potassium, acetate, and phosphate, present at levels up to 0.1 percent if the ethoxylate is not filtered).

In addition, X-77 reportedly can contain trace amounts of ethylene oxide (Valent 1991). Ethylene oxide is considered to be a probable human carcinogen by the International Agency for Research on Cancer (IARC). However, because ethylene oxide is highly volatile, it is not likely to persist in the aquatic environment and probably poses a greater threat to workers handling this material than to aquatic organisms.

#### 3.3 ENVIRONMENTAL EFFECTS

As explained earlier, registration requirements for adjuvants are not as stringent as those for pesticides. Consequently, only limited toxicity information (i.e., mammalian and aquatic organism acute toxicity) is available for most adjuvants. Available toxicity information for the three adjuvants of concern is summarized in Table 1.

# 3.3.1 Aquatic Toxicity

The acute toxicity of alkylphenol ethoxylates generally ranges from 4 to 12 mg/L for fish and from 1 to 100 mg/L for invertebrates (Sivak et al. 1980). Aquatic toxicity is affected by the length of the ethoxylate and alkyl chains on the surfactant molecule. Longer ethoxylate chain lengths result in lower toxicity, while longer alkyl chain lengths result in greater toxicity (Sivak et al. 1980).

Product-specific acute toxicity data for the three surfactants of interest, summarized in Table 1 indicate that the two nonionic alkylphenol ethoxylate products (R-11 and X-77) are generally more toxic to aquatic organisms than is the phosphatidylcholine surfactant (LI-700). In particular, available data suggest that X-77 may be highly toxic to *Daphnia magna*. LI-700 is practically nontoxic to two species of fish (rainbow trout and bluegill sunfish) and to *Daphnia magna*.

Given the typical application rates of these surfactants (i.e., 0.12 to 0.5 gallons per 100 gallons of spray solution), it is unlikely that concentrations in the receiving water environment would exceed the acute toxicity thresholds. Using conservative assumptions (1 foot water depth and maximum application rates for both the adjuvants and the herbicide, i.e., 0.94 gal/acre of glyphosate in a 0.75 percent spray solution), the estimated water column concentration of these adjuvants is approximately 0.2 to 0.3 mg/L, which is up to 3 orders of magnitude lower than the acute toxicity threshold levels.

Mitchell et al. (1987) report that a mixture of Rodeo® (a glyphosate herbicide) and X-77 (31 percent Rodeo®, 0.4 percent X-77, and 69 percent water v:v) was more toxic to rainbow trout than Rodeo® used alone. The 96-hour LC<sub>50</sub> (lethal concentration, mean) values for Rodeo® calculated in terms of the total formulation and for the isopropylamine salt of glyphosate were 1,100 mg/L and 580 mg/L, respectively. In comparison, the LC<sub>50</sub> values for the Rodeo®/X-77 mixture were 680 mg/L and 130 mg/L, respectively, based on the total formulation and the isopropylamine salt of glyphosate. These values indicate that both Rodeo® and Rodeo® mixed with the surfactant X-77 are practically nontoxic to rainbow trout.

Henry (1992) reports similar results with Rodeo® and Rodeo®/X-77 mixtures used on *Chironomus* spp. (midge larvae), *Daphnid* (water flea), *Hyalella azteca* (scud), and *Nephelopsis obscura* (leech). Although X-77 was generally more toxic than the Rodeo® alone, no synergistic effects were observed when the two chemicals were combined. Toxic effects were simply additive, with the Rodeo®/X-77 mixture exhibiting greater toxicity to all four aquatic species than Rodeo® alone:

		LC <sub>50</sub> (mg/L)	
Species	Rodeo®	Rodeo®/X-77	X-77
Midge	1,308	293	10
Water flea	545	130	2
Scud	727	213	6
Leech	1,157	201	11

These data indicate that Rodeo® and Rodeo®/X-77 mixtures are practically nontoxic to aquatic organisms while X-77 alone is moderately toxic. The Rodeo®/X-77 mixture contained Rodeo®, X-77, and Chem-Trol® (a drift retardant) in proportions of 29:1:3 by volume.

Sublethal effects on aquatic organisms have been observed with other nonionic surfactants (i.e., linear alkylbenzene sulfonates and alcohol ethoxylates) at concentrations of 0.5 mg/L (Sivak et al. 1980). These concentrations are below the acute toxicity levels for these surfactants. Sublethal effects observed in fish include impaired swimming activity,

altered breathing rate, and opercular movement. Sublethal effects, such as reduced swimming activity, reduced heart rate, inhibition of siphon retraction, reduced burrowing activity, inhibition of formation of byssal threads, and intestinal damage, have also been reported in aquatic invertebrates at concentrations greater than 1 mg/L of linear alkylbenzene sulfonates and alcohol ethoxylates (Sivak et al. 1980). However, no information on sublethal effects is available for the alkylphenol ethoxylates.

## 3.3.2 Mammalian Toxicity

Oral and dermal acute toxicity data for the three adjuvants of interest are summarized in Table 7. All three adjuvants are classified as practically nontoxic based on rat and rabbit studies. Although no product-specific data are available, chronic toxicity studies using other alkylphenol ethoxylates administered at doses of 1,000 mg/kg/day over a 2-year period to rats and dogs showed no significant toxicity (Sivak et al. 1980).

Both X-77 and LI-700 are rated as system corrosive based on eye irritation in rabbits. No eye irritation rating is provided for R-11. LI-700 is also rated corrosive based on dermal irritation (rabbit).

## 3.4 SUMMARY

Because adjuvants are not regulated under FIFRA, little information is available concerning the environmental fate and effects of R-11, LI-700, and X-77 surfactants. Surfactants are typically soluble in water. Based on their chemical composition, it is expected that R-11 and X-77 are more soluble than LI-700. In addition, because surfactants characteristically concentrate at interfaces, these products may be expected to accumulate primarily at the water surface.

Data for other, similar surfactants indicate that these products are subject to biodegradation. Degradation to the extent that the surfactant characteristics are no longer evident occurs fairly rapidly. However, complete breakdown of the component hydrophilic and hydrophobic units may proceed more slowly. Intermediate degradation products include the relatively low toxicity polyethylene glycol and more highly toxic short-chain ethoxylates. Insufficient data are available to assess potential impacts from these intermediates.

Table 7. Physicochemical characteristics adjuvants used with aquatic herbicides

	R-11	LI-700	X-77
CAS Number	9036-19-5 <u>1</u> /		
Manufacturer	Wilbur-Ellis	T1 1 T. 1	T7 1 T7 0 1
Application Rate (qt/100 gal)	whour-ems	Loveland Ind.	Valent U.S.A.
		0.5-2	0.25-2
TOXICITY DATA (LC <sub>50</sub> ) (Concer	itrations in ppm)		
Fish			
Channel catfish 2/			4.42/
Rainbow trout <sup>2/</sup>	$3.8\frac{3}{2}$	130 <sup>3/</sup>	$4.2^{3/}$
Bluegill sunfish <sup>7</sup>	4.23/	$210^{3/}$	4.33/
Tovicity Pating	36.1		5.54
Toxicity Rating	Moderately toxic	Practically nontoxic	Moderately toxic
Aquatic invertebrates			
Daphnia magna <sup>6/</sup>	$19^{3/}$	170 <sup>3</sup> /	12/
			2 <u>3</u> /
7/			$1.4-2.6^{5/2}$
Hyalella azteca <sup>½</sup> Nephelopsis obscura <sup>½</sup>			4-75/
Chironomus spp. 6/			8-16 <sup>5</sup> /
Chironomus spp			7-14 <sup>5</sup> /
			8.6 <sup><u>8</u>/</sup>
Toxicity Rating	Slightly toxic	Practically nontoxic	Slightly toxic to highly toxic
Marine organisms Grass shrimp <sup>7/</sup>			10 <sup>2</sup> /
Toxicity Rating			Moderately toxic
Mammals			Wiodelately toxic
Oral	•		
Rat			
	NΙΛ	> 5000	> 5000
Rabbit	NA 5840 <sup>9/</sup>	>5000 NA	>5000
	5840 <sup>9/</sup>	NA	NA
Toxicity Rating			
Toxicity Rating Dermal	5840 <sup>9/</sup>	NA	NA
Toxicity Rating Dermal Rat	5840 <sup>2</sup> / Practically nontoxic NA	NA	NA
Toxicity Rating Dermal	5840 <sup>9</sup> / Practically nontoxic	NA Practically nontoxic	NA Practically nontoxic
Toxicity Rating Dermal Rat	5840 <sup>2</sup> / Practically nontoxic NA	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000
Toxicity Rating Dermal Rat Rabbit Primary Irritation Index	5840 <sup>2</sup> / Practically nontoxic  NA 13000 <sup>2</sup> / NA	NA Practically nontoxic 5000	NA Practically nontoxic NA
Toxicity Rating Dermal Rat Rabbit Primary Irritation Index Blank spaces indicate data not avail	5840 <sup>9</sup> / Practically nontoxic  NA 13000 <sup>9</sup> / NA able	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000
Toxicity Rating  Dermal Rat Rabbit  Primary Irritation Index  Blank spaces indicate data not avail  1/ For octylphenoxypoly(ethox	5840 <sup>9</sup> / Practically nontoxic  NA 13000 <sup>9</sup> / NA able	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000
Toxicity Rating  Dermal Rat Rabbit  Primary Irritation Index  Blank spaces indicate data not avail  1/ For octylphenoxypoly(ethox	5840 <sup>9</sup> / Practically nontoxic  NA 13000 <sup>9</sup> / NA able	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000
Toxicity Rating  Dermal Rat Rabbit  Primary Irritation Index  Blank spaces indicate data not avail  1/ For octylphenoxypoly(ethox 2/ Bruce 1992 pers. comm.  3/ Monsanto no date	5840 <sup>9</sup> / Practically nontoxic  NA 13000 <sup>9</sup> / NA able	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000
Toxicity Rating  Dermal Rat Rabbit  Primary Irritation Index  Blank spaces indicate data not avail  1/ For octylphenoxypoly(ethox 2/ Bruce 1992 pers. comm.  3/ Monsanto no date  4/ Watkins et al. 1985  5/ Henry 1992	5840 <sup>9</sup> / Practically nontoxic  NA 13000 <sup>9</sup> / NA able	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000
Toxicity Rating  Dermal Rat Rabbit  Primary Irritation Index  Blank spaces indicate data not avail 1/ For octylphenoxypoly(ethox 2/ Bruce 1992 pers. comm. 3/ Monsanto no date 4/ Watkins et al. 1985 5/ Henry 1992 6/ 48-hr acute toxicity tests	5840 <sup>9</sup> / Practically nontoxic  NA 13000 <sup>9</sup> / NA able	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000
Toxicity Rating  Dermal Rat Rabbit  Primary Irritation Index  Blank spaces indicate data not avail 1/ For octylphenoxypoly(ethox 2/ Bruce 1992 pers. comm. 3/ Monsanto no date 4/ Watkins et al. 1985 5/ Henry 1992 6/ 48-hr acute toxicity tests 7/ 96-hr acute toxicity test	5840 <sup>9</sup> / Practically nontoxic  NA 13000 <sup>9</sup> / NA able	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000
Toxicity Rating  Dermal Rat Rabbit  Primary Irritation Index  Blank spaces indicate data not avail 1/ For octylphenoxypoly(ethox 2/ Bruce 1992 pers. comm. 3/ Monsanto no date 4/ Watkins et al. 1985 5/ Henry 1992 6/ 48-hr acute toxicity tests	5840 <sup>9</sup> / Practically nontoxic  NA 13000 <sup>9</sup> / NA able	NA Practically nontoxic 5000 NA	NA Practically nontoxic  NA >5000

Acute toxicity information based on limited studies with fish and aquatic invertebrates indicates that X-77 and R-11 are more toxic than LI-700. X-77 and R-11 are moderately toxic to fish and slightly toxic to highly toxic to aquatic invertebrates. LI-700 is practically nontoxic to both fish and aquatic invertebrates. Mammalian studies indicate that these products are practically nontoxic to rats and rabbits. However, no data exist to evaluate avian toxicity of these products.

## 4.0 PENDING REGISTRATION FOR AQUATIC USE - TRICLOPYR

### 4.1 BACKGROUND INFORMATION

An aquatic use label for Garlon 3A (triclopyr as the triethylamine [TEA] salt) was submitted to EPA for registration in November 1990. The registration status for aquatic use of triclopyr is still pending and is expected to require at least one more year (R. Taylor personal communication 1992). While this label is being reviewed, there is a federal Experimental Use Permit (EUP) for its use in Washington and 22 other states. DowElanco, the manufacturer of Garlon, has developed an extensive database on triclopyr in aquatic systems, including uses on emergent plants.

Tryclopyr induces characteristic auxin-type responses in growing plants. It is absorbed by leaves and roots and is readily translocated throughout the shoot and root systems. Foliar applications have achieved maximum efficacy when applied after full leaf development and when soil moisture is adequate for normal plant growth.

Demonstration trials for the control of purple loosestrife in Washington with Garlon 3A were established on mature plants in 1988. The studies were conducted by the Bureau of Reclamation and Columbia Irrigation District. These trials showed that Garlon 3A has potential for controlling purple loosestrife selectively when growing around desirable wetland/ditchbank plant species. Further trials have defined the optimal window for applications, optimum rates, and continued program management options. These studies indicate that a comprehensive management program will be necessary for the control of purple loosestrife. One application of any technique or herbicide will not be sufficient to remove the threat of this plant to wetlands.

## 4.2 ENVIRONMENTAL FATE AND TRANSPORT

Triclopyr is considered moderately mobile in soils. In one study, soil organic carbon partitioning coefficients ( $K_{oc}$ s) for the TEA salt ranged from 12 to 78. This study used 12 different soils with organic carbon contents ranging from 0.081 to 21.7 percent (GEIR 1985). In the same study, trichloropyridinol, the major metabolite of triclopyr, appeared

less mobile than triclopyr.  $K_{oc}$ s for trichloropyridinol in three unidentified soil types ranged from 114 to 156.

In a laboratory study of triclopyr, between days 11 and 15, 75 to 80 percent of the applied triclopyr leach through a 12-inch sandy loam soil column with a low organic matter content (0.62 percent) (GEIR 1985). Trichloropyridinol required nearly twice as much water as triclopyr to elute.

In a field study, Garlon 3A was applied at a rate of 3 gallons per acre (9 lbs/acre) to 6 soils ranging from clays to loamy sands. The amount of rainfall during this study was considered normal but was not specified. During days 28 to 56 after the application, small amounts of tricloypr and its metabolites were found in the 6 to 12 inch and 12 to 18 inch soil layers (GEIR 1985, U.S. EPA 1984).

Triclopyr exhibited less mobility in another field study in which the herbicide was applied to sandy loam soil at a rate of 0.6 lb/acre. Over a three-month period with a normal but unspecified amount of rainfall, troclypr was never detected below the top 10 inches of soils. As part of this study, the same soil type was used in a laboratory study and triclopyr was applied at a rate of 0.6 and 6.0 lbs/acre. Rainfall was simulated at a rate of 1 inch per week for 5 weeks. Triclopyr was not detected below the top 4 inches of soil. These results may be a function of a short persistence of triclopyr, rather than an indication of low mobility (Massachusetts DFA and DEP 1991).

#### 4.3 ENVIRONMENTAL PERSISTENCE IN SOILS

Degradation of triclopyr in soils is primarily due to microbial degradation. Under anaerobic conditions, degradation may be 5 to 8 times slower than under aerobic conditions. Chemical hydrolysis and volatilization from soil are not thought to be appreciable degradation mechanisms for triclopyr (GEIR 1985, U.S. EPA 1984).

Degradation rates of triclopyr in soils are variable and may depend on soil and climatic conditions. Under certain conditions, the half-life of triclopyr may be relatively short. For example, a half-life of 10 days in silty clay loam was reported by the Dow Chemical Company (Dow 1983). In another study, a half-life of 14 to 16 days was estimated for triclopyr applied aerially at a rate of 10 lbs/acre to a West Virginia watershed (U.S. EPA

1984). In a Massachusetts field study, a 10-day half-life of triclopyr was reported from 0.6 and 6.0 lbs/acre application rates (Massachusetts DFA and DEP 1991).

Other studies, however, suggest a longer persistence of triclopyr in soil. A laboratory study in which loam was maintained at 95°F with moisture at field capacity indicated a 46-day half-life for triclopyr in loam (Dow 1983). An average triclopyr half-life of 30 days in soil has also been reported (Dow 1983), while the Herbicide Handbook (1983) has reported a 46-day average half-life for triclopyr. Half-lives for triclopyr in soil may also vary with temperature. At temperatures between 25 and 35°C, a half-life of less than 50 days in soil was reported, while at 15°C, a triclopyr half-life was between 79 and 156 days (GEIR 1985).

## 4.4 ENVIRONMENTAL PERSISTENCE IN WATER

TBBE, the butoxyethyl ester of triclopyr, degrades rapidly in water to triclopyr acid. Photolysis is the principal degradation pathway and hydrolysis also contributes. Photolysis half-lives for the ester in water range from 1.5 to 2 days (McCall and Gavit 1986, Dow 1989). Hydrolysis half-lives are dependent upon water pH and temperature and range from 0.06 day to 208 days; they decrease with increasing temperature and pH (Hamaker 1977). With the exception of the Hamaker (1977) study and a slow breakdown at pH 5, most studies indicate that TBEE in water is degraded relatively rapidly (Massachusetts DFA and DEP 1991).

The acid half-life is reported to range from 2.1 hours at the water's surface in summer to 14 hours at a depth of 1 meter in winter (McCall and Gavit 1986). TCP (3,5,6-trichloro-2-pyridinol), the principle decay product of the acid, also is short-lived in the aquatic environment, with a half-life ranging from minutes to 1 day (Hamaker 1977).

## 4.5 ENVIRONMENTAL TOXICITY

Both triclopyr and Garlon 3A herbicide have very low toxicity to aquatic invertebrates. Table 8 contains the 96 hour LC<sub>50</sub> values for fish and Daphnia. The effect of prolonged exposure to Garlon 3A herbicide in water was evaluated with fathead minnows and Daphnia. These tests indicated no effects on fathead minnow embryo hatchability or larval development during a 31-day exposure to 202 mg/L of Garlon 3A herbicide.

Table 8. Fish and Invertebrate 96 hour LC<sub>50</sub> values for triclopyr.

	Triclopyr	Triclopyr TEA Salt	Triclopyr Butoxyl Ethyl Ester
Bluegill	148 mg/L	891 mg/L	0.87 to 1.5 mg/L
Rainbow Trout	117 mg/L	552 mg/L	0.74 to 1.3 mg/L
Coho Salmon	-		1.3 mg/L
Fathead Minnow	_	248 mg/L	2.2 mg/L
Daphnia magna (water fleas)	133 mg/L	775 mg/L	2.2 to 10 mg/L

Triclopyr has very low toxicity to birds. Consequently, environmental exposures should not result in any significant hazards to birds.  $LC_{50}$  values from eight-day dietary studies and  $LD_{50}$  values are indicated in Table 9. In a one-generation reproduction study, bobwhite quail and mallard ducks exposed to 100, 200, and 500 ppm of triclopyr in their diet showed no symptoms of toxicity, behavioral abnormalities, or reproductive impairment.

Table 9. Avian eight-day dietary  $LC_{50}$  and acute oral  $LD_{50}$  values for triclopyr.

	Triclopyr	Triclopyr TEA Salt	Triclopyr Butoxyl Ethyl Ester
Mallard Duck	>5,600 ppm	>10,000 ppm	>10,000 ppm
Bobwhite Quail	2,935 ppm	11,622 ppm	9,026 ppm
	Acute	Oral LD <sub>50</sub>	
Mallard Duck	1,698 mg/kg	3,176 mg/kg	>4,640 mg/kg

## 5.0 EFFICACY AND PRACTICALITY OF APPLICATION METHODS

The effectiveness and practicality of aquatic herbicides in the control of noxious weeds is highly dependent on the proper selection of herbicide formulation and application method. Aquatic herbicides are available in both liquid and dry formulations. Liquids, such as Rodeo® and Weedar 64® are usually a mixture of the active ingredient, solvents, emulsifiers, and other diluents. Dry formulations are primarily granules or pellets that are impregnated with the active ingredient. To ensure maximum effectiveness and to minimize effects on non-target organisms, all forms of herbicides must be applied as specified on the herbicide label. This can be accomplished only if the proper application equipment is used and if the equipment is calibrated properly.

The following sections discuss herbicide application using helicopter, wicking, back-pack sprayer, boat, and injection. Advantages and disadvantages of each technique in a given situation, including relative requirements for labor and fuel, are presented.

#### 5.1 HELICOPTER

Helicopters are widely used to spray herbicides in both terrestrial and aquatic environments. Helicopter applications allow for a more controlled and directed spray than is possible using fixed-wing aircraft. Typical spray apparatus consists of a boom with multiple nozzles for broadcast delivery of the herbicide. Different boom designs and nozzle configurations are available, and are selected as appropriate for the site to be sprayed.

An alternative to a helicopter with a boom is a helicopter with ball. Use of a spray ball rather than boom allows the potential for drift to be minimized. The ball apparatus, which contains a spray nozzle system, hangs from the helicopter on a stem. The helicopter can hover over an area and use the ball to spray a small clump of noxious plants. This technique may be particularly appropriate when a spray site is located near a sensitive ecological habitat or human population.

Helicopters are limited to using the tank mix method for preparing the herbicide to be sprayed. A tank mix is prepared in which the herbicide and the diluent, usually water, are mixed in a tank and the mixture is applied to the weeds. In addition to aerial applications, tank mix methods are often used when applying herbicide by boat, tractor, or back-pack sprayer.

Helicopter mix applications require the proper functioning of several key components: tank, agitation system, hoses, pumps and nozzles. A 50-150 gallon fiberglass tank is generally used, which has graduations on the side indicating the volume at that level. Good agitation is important for maintaining a uniform spray mixture and for mixing of adjuvants such as surfactants or polymers. Both hydraulic and mechanical agitators are commonly used.

Hoses which have chemically resistant inner and outer layers are used. Two materials widely used for hoses are ethylene vinyl acetate (EVA) and ethylene propylene dione monomer (EPDM). A pressure hose must be strong enough to withstand the maximum pressure within its length without bursting. Most of the pumps used for applying liquids for controlling weeds are of five general types: roller, piston, centrifugal, diaphragm and gear. The selection of pump is dependent on the application, since each pump has specific capabilities and limitations.

The spray nozzle provides three basic functions: forms the spray pattern, determines the droplet size, and meters the herbicide flow rate. The number of nozzles appropriate for use in aquatic weed control is determined by application method. Aerial applications normally use hollow cone or flat fan nozzles to improve coverage with the smaller volume of spray solution applied per acre. A specialized aerial boom designed to produce a large droplet size at low pressure and low volume is the microfoil boom.

The major advantages to helicopter application are the ability to quickly apply herbicide to a large area. If correct formulation procedures are followed the proper equipment is selected and applications are made only when weather conditions are favorable, then the potential for drift can be minimized. The potential for drift can be minimized further by using the helicopter with ball.

### **5.2 BOAT**

Boats with outboard motors or airboats can be used as the herbicide delivery method for spray applications as well as wicking applications. Two methods are suitable for preparing the herbicide to be sprayed from a boat: 1) A tank mix; or 2) The herbicide is metered into the suction side of a pump at the rate needed to apply the correct amount per acre. The diluent needed to ensure adequate coverage is drawn directly from the body of water being treated.

The tank mix method is suitable for treating relatively small areas, or when mixing several herbicides. When large areas are treated, many applicators find it more efficient to use the "direct metering" method to reduce the time spent refilling the tank.

The key component requirements for a tank mix application are similar to those for helicopter application. Nozzles used for spraying surface, emersed and ditchbank species typically provide a high flow rate (3 to 6 gal/minute), a straight stream, and a large droplet size. This arrangement ensures thorough wetting of the target vegetation with minimum spray drift.

Spray applications using boats are particularly appropriate when the areas surrounding the target plants make an aerial application difficult, either because of the ecological habitat or public sensitivity. Boat applications allow for a more specific application of the herbicide, and reduce the possibility of drift or over-spray. When large areas need to be treated, boat applications can take longer than aerial applications, but the public perception advantages may outweigh the additional time and labor required.

#### 5.3 BACK-PACK SPRAYER

The use of back-pack spray herbicide applications is ideal for treatment of relatively small areas where controlled application is desired. Typical commercial back pack spray equipment consists of a hand held wand with one or two solid cone nozzles attached to a  $CO_2$  pressurized backpack sprayer. Fan nozzles are also used with backpack sprayers. The spray is typically applied to individual plants until the foliage is visibly wet. The operator is usually on foot, but could be in a boat, as well.

In a comparison of back-pack spray with wicking in a terrestrial environment, both techniques provided effective control of the pest species without damage to surrounding native plants (Ralphs et al. 1991). However, the back-pack sprayer was almost twice as rapid as the wiper, and the application was easier. Precautions should be taken with any spray technique to minimize spray drift and over-spray. Spray drift is a disadvantage of this herbicide application method, because the herbicide could inadvertently affect desirable vegetation or sensitive ecosystems. Similarly, overspray could result in the introduction of greater than negligible amounts of herbicide into nearby water or surrounding soils or vegetation.

#### 5.4 WICKING

Wicking or wiping is the direct application of herbicide onto the plant surface using rope, paint rollers, absorbent foam rubber, carpet or any absorbent material which can transfer the herbicide onto the leaf surface. This technique is more labor intensive than spraying, but can be very effective and may require less herbicide to achieve control. Rodeo® used in conjunction with wicking has been successful when used in the proportions of 1 part Rodeo® to 2 parts water/surfactant and applied carefully.

Wicking minimizes the potential for impact on nontarget organisms, because of the preciseness of the herbicide application onto the noxious plant. There is no opportunity for overspray. Wicking also allows taller species to be selectively removed, while lower species are left undamaged. However, to achieve control in some species, it is necessary to cover the entire plant with herbicide, which may require several passes across the plants from different directions.

### 5.5 INJECTION

Woody vegetation can be controlled by injection application of herbicide. The herbicide must be applied with suitable equipment which penetrates the cambium. Rodeo® is used frequently with the E-Z-Ject system sold by Monsanto for tree injection.

For Rodeo® application, about 1 ml of herbicide is used per 2-3 inches of trunk diameter. This may be best achieved by applying 25 to 100 percent concentration of material either to a continuous frill around the tree or as cuts evenly spaced around the tree below all branches. Care should be taken to avoid having runoff from frill or cut areas. For

Weedar® application, 1 to 2 ml of concentrate per injection should be used, and one injection per inch of trunk diameter should be made. Alternately, a dilute mixture of 1 gallons of Weedar® to 19 gallons of water may be used. Applications should be made during periods of active growth and full leaf expansion.

The primary advantage of injection is the direct application of herbicide to the target plant, with little potential for nontarget plant impact. This is a very effective technique for susceptible species. It is however, time consuming and labor intensive, and thus suitable for use in relatively small areas.

## 5.6 OTHER METHODS

Cut stump applications should be considered as a potential control alternative for woody species. This technique involves the treatment of freshly cut stumps of trees and resprouts with herbicide. The herbicide should be applied using suitable equipment to ensure coverage of the entire cambium.

Rodeo® works very well on a variety of woody species when a 50 to 100 percent solution is applied to a freshly cut surface. For best results, trees should be cut during periods of active growth and full leaf expansion. The technique also allows a very controlled application of herbicide, but is labor and time consuming. The Weedar® label does not provide cut stump application instructions or warnings.

## 6.0 REFERENCES

- Ahrens, J.F. 1974. Selectivity of glyphosate and asulam in ornamental plantings and christmas trees. Proc. Northeast. Weed Sci. Soc. 28:361-368.
- Aly, O.M. and S.D. Faust. 1964. Studies on the fate of 2,4-D and ester derivatives from natural waters. J. Agr. Food Chem. 12(b):541-546 (as cited in Shearer and Halter 1980).
- Arthur D. Little, Inc. 1977. Human safety and environmental aspects of major surfactants. NTIS PB 301 193/9ST (as cited by Sivak et al. 1980).
- Baird, D.D., R.P. Upchurch, W.B. Homesley, and J.E. Franz. 1971. Introduction of a new broadspectrum postemergence herbicide class with utility for herbaceous perennial weed control. Proc. North Cent. Weed Control Conf. 26:64-68.
- Balajee, S. and A. Mahadevan. 1990. Dissimilation of 2,4-dichlorophenoxy acetic acid by Azotobacter chroococcum. Xenobiotica 20(6):607-617.
- Balogh, G.R. 1986. Ecology, distribution, and control of Purple Loostrife (*Lythrum salicaria*) in northwest Ohio. Thesis submitted to Ohio State University.
- Balogh, J.C. and W.J. Walker (eds). 1992. Golf course management and construction, environmental issues. Lewis Publishers, Boca Raton, FL.
- Balthazar, T.M. and L.E. Hallas. 1986. Glyphosate-degrading microorganisms from industrial activated sludge. Appl. Environ. Microbiol. 51:432-434 (as cited by Reinert and Rodgers 1987).
- Barriuso, E., C. Feller, R. Calvet, and C. Cerri. 1992. Sorption of atrazine, terbutryn, and 2,4-D herbicides in two Brazilian Oxisols. Geoderma 53:155-167.
- Birch, R.R. 1984. Biodegradation of nonionic surfactants. JAOCS 61:340-343 (as cited by Swisher 1987).

- Birmingham, B.C. and B. Colman. 1985. Persistence and fate of 2,4-D butoxyethanol ester in artificial ponds. J. Environ. Qual. 14(1):100-104.
- Bloom, Jill. 1992. Review Manager, Office of Pesticide Programs, U.S. Environmental Protection Agency. Personal Communication.
- Bollag, J.M., Y. Liu, and R.D. Minard. 1980. Cross-coupling of phenolic humus constituents and 2,4-dichlorophenol. Soil Sci. Soc. America J. 44(1):52-56.
- Brandt, E.J. 1984. A health and environmental report on Rodeo® herbicide. Bull. No. 2. Monsanto Agricultural Products Company, St. Louis, MO. 3 pp. (as cited by Reinert and Rodgers 1987).
- Breeze, V.G. and E. van Rensburg. 1991. Vapour of the free acid of the herbicide 2,4-D is toxic to tomato and lettuce plants. Environmental Pollution 72:259-267.
- Bronstad, J.O. and H.O. Friestad. 1985. Behavior of glyphosate in the aquatic environment. In: The Herbicide Glyphosate. Edited by E. Grossbard and D. Atkinson. Butterworths, London.
- Bruce, E. June 11, 1992. Personal communication (letter to R.J. Stevens concerning aquatic toxicity of Valent X-77 spreader). Valent U.S.A. Corporation, Walnut Creek, CA.
- Buhl, K.J. and N.L. Faerber. 1989. Acute toxicity of herbicides and surfactants to larvae of the midge Chironomus riparius. Arch. Environ. Contam. Toxicol. 18:530-536.
- Burrill, L.C., R.D. William, R. Parker, C. Beerboom, R.H. Callihan, C. Eberlein, and D.W. Morishita. 1992. Pacific Northwest Weed Control Handbook. Oregon State University, Corvallis, OR.
- Chakrabarty, A.M. 1982. Biodegradation and detoxification of environmental pollutants. CRC Press, Inc., Boca Raton, FL.

- Chase, W.L. 1985. Personal Communication (letter to Ms. Bernalyn McGaughey, Washington Pest Management Council with partial copy of report prepared by Dow Chemical). Ortho Chevron Company, Richmond, CA. February 5, 1985.
- Chen, S. and M. Alexander. 1989. Reasons for the acclimation for 2,4-D biodegradation in lake water. J. Environ. Qual. 18:153-156.
- Chiou, C.T., V.H. Freed, D.W. Schmedding, and K.L Kohnert. 1977. Partition coefficient and bioaccumulation of selected organic chemicals. Environ. Sci. Technol. 11:475-478 (as cited in Reinert and Rodgers 1987).
- Comes, R.D., V.F. Bruns, and A.D. Kelley. 1976. Residues and persistence of glyphosate in irrigation water. Weed Sci. 24(1):47-50.
- Conway, R.A., G.T. Waggy, M.H. Spiegel, and R.L. Berglund. 1983. Environmental fate and effects of ethylene oxide. Env. Sci. Technol. 17:707-112 (as cited by Swisher 1987).
- Coombs, Judy. 1992. Reregistration Branch, Office of Pesticide Programs, U.S. Environmental Protection Agency. Personal Communication.
- Cope, O.B., E.M. Wood, and G.H. Wallen. 1970. Some chronic effects of 2,4-D on the bluegill (Lepomis macrochirus). Trans. AM. Fish. Soc. 99:1-12 (as cited in Birmingham and Colman 1985).
- Crockett, Ron. 1992a. Spartina Control Update (draft). Monsanto Company.
- Crockett, Ron. 1992b. Smooth Cordgrass Control Using Rodeo Herbicides. Technical Summary, Monsanto Company.
- Crockett, Ron. 1992c. Product Development Specialists, Monsanto Company.
- Davis, C. 1992. Monsanto response center. Personal communication by telephone with W. Trial, September 21, 1992.
- Dean, J.A. (ed). 1985. Lange's handbook of chemistry. McGraw-Hill, New York, NY. SOW/2-2-93/03554A

- DeLaune R.D. and L.M. Salinas. 1985. Fate of 2,4-D entering a freshwater aquatic environment. Bull. Environ. Contam. Toxicol. 35:564-568 (as cited in DeLaune et al. 1990).
- DeLaune, R.D., R.P. Gambrell, J.H. Pardue, and W.H. Patrick. 1990. Fate of petroleum hydrocarbons and toxic organics in Louisiana coastal environments. Estuaries 13(1):72-80.
- Dow Chemical Company. 1983. Technical Information on Triclopyr, The Active Ingredient of Garlon Herbicides. Technical Data Sheet No. 137-859-483. Dow Chemical Company, Agricultural Products Department, Midland, Michigan. As cited by Pesticide Background Statements, (1984).
- Dow Chemical USA. 1989. Personal Communication. Letter from Dr. Frank A. Kidd to Mr. Ledorte Real. MADFA. Dated 9/21/89.
- Dynamac Corporation. 1988. 2,4-D, its inorganic salts and [X]-2,4-D. Task 2: environmental fate and exposure assessment. Prepared for U.S. Environmental Protection Agency, Dynamac Corporation, Rockville, MD.
- Ebasco Environmental and Herrera. 1992. Noxious Emergent Plant: Environmental Effects of Glyphosate and 2,4-D.
- Edwards, W.M., G.B. Triplett, Jr., and R.M. Kramer. 1980. A watershed study of glyphosate transport in runoff. J. Environ. Qual. 9(4):661-665.
- Feng, J.C. and D.G. Thompson. 1990. Fate of glyphosate in a Canadian forest watershed: 2. Persistence in foliage and soils. J. Agric. Food Chem. 38:1118-1125.
- Feng, J.C., D.G. Thompson, and P.E. Reynolds. 1990. Fate of glyphosate in aCanadian forest watershed: 1. Aquatic residues and off-target deposit assessment.J. Agric. Food Chem. 38:1110-1118.
- Frank, P.A. and R.D. Comes. 1967. Herbicidal residues in pond water and hydrosoil. Weeds 15:210-213 (as cited in Birmingham and Colman 1985).

- Gangstad, E.E. 1982. Dissipation of 2,4-D in large reservoirs. J. Aquat. Plant Mgmt. 20:13-16 (as cited by Reinert and Rodgers 1987).
- Gangstad, E.O. 1986. Freshwater vegetation management. Thomas Publications, Fresno, CA.
- Garnett, R.P. 1991 (unpublished). The control of Spartina on salt marshes and mudflats using Roundup® Pro herbicide: An overview of efficiency and ecotoxicity.
- GEIR (Generic Environmental Impact Report). 1985. Control of vegetation of utilities and railroad rights of way. Pub. by Harrison Biotec, Cambridge, MA.
- Getsinger, Kurt. 1992. Plant Pathologist, Corps of Engineers Waterways Experiment Station. Personal Communication.
- Ghassemi, M., S. Quinlivan, and M. Dellarco. 1982. Environmental effects of new herbicides for vegetation control in forestry. Environ. Int. 7:389-401.
- Gilmore, Mary. 1992. Sales Representative, Monsanto Company. Personal Communication.
- Goldsborough, L.G. and A.E. Beck. 1989. Rapid dissipation of glyphosate in small forest ponds. Arch. Environ. Contam. Toxicol. 18:537-544.
- Gottrup, O., P.A. O'Sullivan, R.J. Schraa, and W.H. VandenBorn. 1976. Uptake, translocation, metabolism and selectivity of glyphosate in Canada thistle and leafy spurge. Weed Res. 16:197-201
- Greer, C.W., J. Hawari, and R. Samson. 1990. Influence of environmental factors on 2,4-dichlorophenoxy acetic acid degradation by Pseudomonas cepacia isolated from peat. Archives of Microbiology pp. 317-322.
- Greer, L.E. and D.R. Shelton. 1992. Effect of inoculant strain and organic matter content on kinetics of 2,4-dichlorophenoxy acetic acid degradation in soil. Applied and Environmental Microbiology 58(5):1459-1465.

- Grover, R. 1973. The adsorptive behavior of acid and ester forms of 2,4-D on soils. Weed Res. 13:51-58.
- Grover, R. and A.E. Smith. 1974. Adsorption studies with the acid and dimethylamine forms of 2,4-D and dicamba. Can. J. Soil Sci. 54:179-186.
- Hamaker, J.W. 1977. Photolysis of Triclopyr ((3,5,6-trichloro-2-pyridinyl) oxyacetic acid) in aqueous solution. GS-1467. Unpublished data of Dow Chemical USA referenced in Woodburn, n.d.
- Hammond, L. 1992. 2,4-D Task Force, personal communication. September 25, 1992
- Hance, R.J. 1976. Adsorption of glyphosate by soils. Pestic. Sci. 7:363-366.
- Harris, C.I and G.F. Warren. 1964. Adsorption and desorption of herbicides by soil. Weeds 12:120-126 (as cited in Hoeppel and Westerdahl 1983).
- Hattula, M.L., V.M. Wasenius, H. Reunanen, and A.U. Artsila. 1981. Acute toxicity of some chlorinated phenols, catechols and cresols to trout. Bull. Environ. Contam. Toxicol. 26:295-298 (as cited by Birmingham and Colman 1985).
- Helling, C.S. 1971. Pesticide mobility in soils II. applications of soil thin-layer chromatography. Soil Sci. Soc. Amer. Proc. 35:737-742.
- Henry, C.J. 1992. Effects of Rodeo® Herbicide on Aquatic Invertebrates and Fathead Minnows. Thesis submitted to South Dakota State University.
- Herbicide Handbook. 1983. Fifth Ed. Handbook of the Weed Science Society of America. Pub. by the Weed Science Society of America. Champaign, Ill.
- Heydens, W.F. 1991. Rodeo<sup>®</sup> herbicide use to control Spartina: Impact of glyphosate on marine and terrestrial organisms. Monsanto Agricultural Products Company. September 1991 (unpublished).

- Hoeppel, R.E. and H.E. Westerdahl. 1983. Dissipation of 2,4-D DMA and BEE from water, mud, and fish at Lake Seminole, Georgia. Water Resources Bulletin 19(2):197-203.
- Holcombe, G.W., J.T. Fiandt, and G.L. Phipps. 1980. Effects of pH increases and sodium chloride additions on the acute toxicity of 2,4-dichlorophenol to the fathead minnow. Water Res. 14:1073-1077 (as cited by Birmingham and Colman 1985).
- Hunter, R., L. Faulkner, T. Kaiserski, D. Antonsen. 1984. Quantitative structure-activity relationships (QSAR) system. Center for Data Systems and Analysis. Montana State University, Bozeman, MT. 32 pp. (as cited by Reinert and Rodgers 1987).
- Huston, B.L. 1972. Identification of three neutral contaminants in production grade 2,4-D. J. Agr. Food Chem. 20:724-727 (as cited in IARC).
- IARC (International Agency Research on Carcinogens). 1982. IARC Monograph: 2,4-D and esters. Lyon, France.
- Khan, S.U. and J.C. Young. 1977. N-nitrosoamine formation in soil from the herbicide glyphosate. J. Agric. Food Chem. 25:1430-1432.
- Kim, C.J. and W.J. Maier. 1986. Acclimation and biodegradation of chlorinated organic compounds in the presence of alternate substrates. Journal WPCF 58(2):157-164.
- Kirk-Othmer. 1983. Encyclopedia of chemical technology. 3d edition. Volume 14. John Wiley and Sons, New York, NY.
- Klingman, G.C., F.M. Aston, and L.J. Noordhoff. 1975. Weed science: principles and practice. John Wiley and Sons, New York, NY (as cited in Westerdahl et al. 1988).
- Kroll, R.B. 1991. Field investigation of the environmental fate of Rodeo® (glyphosate) in two tidal marshes. Technical Report No. 115. Maryland Department of the Environment, Water Management Administration, Standards and Certification Division. August 1991.

- Kuwatsuka, S. and N. Miwa. 1989. Change in population of 2,4-D degraders in the process of 2,4-D degradation in soils under upland and flooded conditions. Soil Sci. Plant Nutr. 35(4):535-543.
- Lashen, E.S., F.A. Blankenship, K.A. Booman, and J.Dupre. 1966. Biodegradation studies on a p-t-octylphenoxypolyethoxyethanol. JAOCS 43:371-376 (as cited by Swisher 1987).
- Lashen, E.S., G.F. Trebbi, K.A. Booman, and J. Dupre. 1967. Biodegradability of nonionic detergents. Soap Chem. Specialties 43(1):55-58, 122-129 (as cited by Swisher 1987).
- Lehninger, A.L. 1975. Biochemistry. 2d edition. Worth Publishers, Inc., New York, NY.
- Little, A.D., Inc. 1977. Human Safety and environmental aspects of major surfacants. NTIS PB 301 193/9ST (as cited by Sivak et al. 1980).
- Loos, M.A. 1975. Phenoxyalkanoic acids. In: Herbicides--chemistry, degradation, and mode of action, Vol. 1, 2nd ed., Kearney, P.C. and D.D. Kaufman (eds) Marcel Dekker, New York, NY (as cited in Chakrabarty 1982).
- MacKenzie, D.L. 1979. Aquatic nuisance control in Ontario, 1975-1979. Ontario Ministry of the Environment Report, Pesticides Control Section, Ontario, Canada (as cited in Birmingham and Colman 1985).
- Malecki, R.A. and T.J. Rawinski. 1985. New methods for controlling purple loostrife. N.Y. Fish Game J. 32:9-19.
- Mann, A.H. and V.W. Reid. 1971. Biodegradation of synthetic detergents evaluation by community trials. II. Alcohol and Alkylphenol ethoxylates. JAOCS 48:588-594 (as cited by Swisher 1987).
- Massachusetts Department of Food and Agriculture (DFA) and Department of Environmental Protection (DEP). 1991. A Review of the Herbicide Triclopyr Pursuant to 333 CMR 11.04(1)(d). Ad Hoc Committee. February 19, 1991.

- McCacken, Hue. 1992. South Columbia Basin Irrigation District. Personal Communication.
- McCall, P.J., and P.D. Gavit. 1986. Aqueous photolysis of Triclopyr and its butoxyethyl ester and calculated environmental decomposition rates. Envtl. Tox. and Chem. 5:879-885.
- McCall, P.J., S.A. Vrona, and S.S. Kelley. 1981. Fate of uniformly carbon-14 ring labeled 2,4,5-trichlorophenoxyacetic acid and 2,4-dichlorophenoxyacetic acid. J. Agric. Food Chem. 29:100-107 (as cited in Reinert and Rodgers 1987).
- Meguro, K., M. Ueno, and K. Esumi. 1987. Micelle formation in aqueous media. pp. 109-184 in: Nonionic Surfactants, Physical Chemistry, Vol. 1. M.J. Schick (ed). Marcel Dekker, Inc., New York, NY.
- Meru, S., K. Liber, K. Solomon, and G. Stephenson. 1990. Persistence and lateral movement of 2,4-dichlorophenoxy acetic acid and picloram on power line rights-of-way. Archives of environmental contamination and toxicology 19:572-577.
- Minnesota Department of Natural Resources (MDNR). 1988. Control and Eradication of Purple Loosestrife.
- Mitchel, D.G., P.M. Chapman, and T.J. Long. 1987. Acute toxicity of Roundup« and Rodeo« herbicides to rainbow trout, chinook, and coho salmon. Bull. Environ. Contam. Toxicol. 39:1028-1035.
- Moia, H. May 28, 1992. Personal communication (telephone conversation with Beth Schmoyer, Herrera Environmental Consultants). Washington Department of Aquaculture, Yakima, WA.
- Monsanto Agricultural Products Company. 1985. Rodeo® herbicide for aquatic vegetation management. Technical manual. 20 pp.
- Monsanto Agricultural Products Company. Undated. Table of LC<sub>50</sub> values for different surfactants.

- Monsanto Company. 1990. Rodeo® aquatic herbicide. Complete directions for use in aquatic and other noncrop sites. March 1, 1990.
- Morris, K. and R. Jarman. 1981. Evaluation of water quality during herbicide applications to Kerr Lake, OK. J. Aquat. Plant Manage. 19:15-18.
- Mount, D.I. and C.E. Stephan. 1967. A method for establishing acceptable toxicant limits for fish-malathion and the butoxyethanol ester of 2,4-D. Trans. Am. Fish Soc. 96:185-193 (as cited in Birmingham and Colman 1985).
- Muller, M.M., C. Rosenberg, H. Siltanen, and T. Wartiovaara. 1981. Fate of glyphosate and its influence on nitrogen cycling in two Finnish agricultural soils. Bull. Environ. Contam. Toxicol. 27:724-730.
- Newton, M., K.M. Howard, B.R. Kelpsas, R. Danhaus, C.M. Lottman, and S. Dubelman. 1984. Fate of glyphosate in an Oregon USA forest ecosystem. J. Agric. and Food Chem. 32:1144-1151.
- Nicholls, P.H. and A.A. Evans. 1991. Sorption of ionizable compounds by field soils. Part 2: Cations, bases and zwitterions. Pestic. Sci. 33:331-345.
- O'Keefe, M.G. 1985. The evaluation of glyphosate degradation in a bird sanctuary.

  Monsanto internal report. (as cited by Garnett 1991.)
- Otto, N.E., J.C. Pringle, D. Sisneros. 1983. Herbicidal residues and environmental effects from the experimental application of two 2,4-D formulations to control Eurasian watermilfoil. REC-ERC-83-1 (as cited by Reinert and Rodgers 1987).
- Paris, D.F., W.C. Steen, G.L. Baughman, J.T. Burnett Jr. 1981. Second-order model to predict microbial degradation of organic compounds in natural waters. Applied Environ. Microbiol. 41:603-609 (as cited by Reinert and Rodgers 1987).
- Quilty, S.P. and M.J. Geoghan. 1976. The degradation of glyphosate in peat. Proc. Soc. Gen. Micro. 3:129.

- Ralphs, M.H., L.V. Mickelsen, J.O. Evans, and S.A. Dewey. 1991. Selective application of Glyphosate for control of Larkspurs (*Delphinium* spp.). Weed Technology. 5(1):229-231.
- Rawinski, T.J. 1982. The ecology and management of purple loostrife (*Lythrum salicaria* L.) in central New York. M.S. Thesis. Cornell University, Ithaca, N.Y. ix + 88 pp.
- Reinert, K.H. and J.H. Rodgers. 1987. Fate and persistence of aquatic herbicides. Review of Environ. Contamination and Toxicology. Edited by G.W. Ware, Springer-Verleg, New York. 98:61-98.
- Robson, T.D. 1968. Some studies of the persistence of 2,4-D in natural surface waters. Proc. 9th British Weed Control Conference, pp 404-408 (as cited by Reinert and Rodgers 1987).
- Roy, D.N., S.K. Koner, S. Banerjee, D.A. Charles, D.G. Thompson, and R. Prasad. 1989. Persistence, movement, and degradation of glyphosate in selected Canadian boreal forest soils. J. Agric. Food Chem. 37:437-440.
- Rueppel, M.L., B.B. Brightwell, J. Schaeffer, and L.T. Marvel. 1977. Metabolism and degradation of glyphosate in soil and water. J. Agric. Food Chem. 25:517-528.
- Sacher, R.M. 1978. Safety of Roundup® in the aquatic environment. pp. 315-322 in: Proc. EWRS 5th Symp. on Aquatic Weeds.
- Schultz, D.P. and E.O. Gangstad. 1990. Dissipation of residues of 2,4-D in water, hydrosoil, and fish, In: Natural resource management of water and land. Gangstad, E.O (ed), Van Nostrand Reinhold, New York, NY.
- Schultz, D.P. and P.D. Harman. 1974. Residues of 2,4-D in pond waters, mud, and fish. Pestic. Monitor. J. 8:173-179 (as cited in Birmingham and Colman 1985).
- Schwartz, H.G., Jr. 1967. Microbial degradation of pesticides in aqueous solutions. J. Water Poll. Contr. Fed. 39:1701-1714 (as cited in Shearer and Halter 1980).

- Schoen-Nesser R. 1992. Personal Communication. Phone Conservation with Scott Luchessa, Herrera Environmental Consultants. Washington State Department of Agriculture, Olympia, WA.
- SCS (Soil Conservation Service). 1989. Washington state water quality guide:

  Integrating water quality and quantity into conservation planning. U.S. Department of Agriculture, Soil Conservation Service.
- Shaner, D.L. and J.L. Lyon. 1980. Early effects of glyphosate on free amino acid levels in bean leaves. Abstr. Weed Sci. Soc. Am. 1980:93.
- Shearer, R. and M. Halter. 1980. Literature review of four selected herbicides: 2,4-D, dichlorobenil, diquat, and endothall. Prepared for Municipality of Metropolitan Seattle, WA.
- Shiu, W.Y. K.C. Ma, D. Mackay, J.N. Seiber, and R.D. Wauchope. 1990. Solubilities of pesticide chemicals in water, Part II: data compilation. Reviews of Environmental Contamination and Toxicology 116:15-187.
- Sivak, A., M. Goyer, J. Perwak, and P. Thayer. 1980. Environmental and human health aspects of commercially important surfactants. pp. 161-188 in: Solution Behavior of Surfactants, Theoretical and Applied Aspects, Vol. 1. K.L. Mittal and E.J. Fendler (eds). Plenum Press, New York, NY.
- Smith, A.E. 1972. The hydrolysis of 2,4-dichlorophenoxyacetate esters to 2,4-dichlorophenoxyacetic acid in Saskatchewan soils. Weed Res. 12:364-372 (as cited in Birmingham and Colman 1985).
- Smith, A.E. 1978. Relative persistence of di- and trichlorophenoxyalkenoic acid herbicides in Saskatchewan soils. Weed Res. 18:275-279 (as cited in Birmingham and Colman 1985).
- Smith, A.E. 1979. Soil persistence experiments with <sup>14</sup>C-2,4-D in herbicidal mixtures, and field persistence studies with tri-allate and trifluralin both singly and combined. Weed Research 19:165-170 (as cited in Smith 1989).

- Smith, A.E. 1980. Persistence studies with <sup>14</sup>C-2,4-D in soils previously treated with herbicides and pesticides. Weed Research 20:355-359 (as cited in Smith 1989).
- Smith, A.E. 1989. Degradation, fate, and persistence of phenoxyalkanoic acid herbicides in soil. Rev. Weed Sci. 4:1-24.
- Smith, A.E. and A.J. Aubin. 1991. Metabolites of [14C]-2,4-dichlorophenoxy acetic acid in Saskatchewan soils. J. Agric. Food Chem. 39:2019-2021.
- Smith, A.E., A.J. Aubin, and V.O. Biederbeck. 1989. Effects of long-term 2,4-D and MCPA field applications on soil residues and their rates of breakdown. J. Environ. Qual. 18:299-302.
- Smith, G.E. and B.G. Isom. 1967. Investigation of effects of large-scale applications of 2,4-D on aquatic fauna and water quality. Pestic. Monitor. J. 1(3):16-21 (as cited in Birmingham and Colman 1985).
- Sprankle, P., W.F. Meggitt, and D. Penner. 1975a. Rapid inactivation of glyphosate in the soil. Weed Science 23:224-228.
- Sprankle, P., W.F. Meggitt, and D. Penner. 1975b. Adsorption, mobility, and microbial degradation of glyphosate in the soil. Weed Science 23:229-234.
- Sutton, R.F. 1978. Glyphosate herbicide: an assessment of forestry potential. For Chron. 54:24-28.
- Swisher, R.D. 1987. Surfactant biodegradation. 2d edition. Marcel Dekker, New York, NY.
- Tadros, T.F. 1984. Surfactants. Academic Press, New York, NY.
- Taylor, Robert. 1992. Aquatic Group, U.S. Environmental Protection Agency. Personal Communication.

- Thibideaux, L.J. 1979. Chemodynamics-environmental movement of chemicals in air, water, and soil. Wiley-Interscience, New York, NY (as cited in Reinert and Rodgers 1987).
- Tiedje, J.M and M. Alexander. 1969. Enxymatic cleavage of the ether bond of 2,4-dichlorophenoxyacetate. J. Agric. Food Chem. 17:1080.
- Tooby, T.E. 1985. Fate and biological consequences of glyphosate in the aquatic environment; pp. 206-217 in: The Herbicide Glyphosate. Edited by E. Grossbard and D. Atkinson. Butterworths, London.
- Torstensson, L. and A. Aamisepp. 1977. Detoxification of glyphosate in soil. Weed Res. 17:209-212.
- Torstensson, L. 1985. Behaviour of glyphosate in soils and its degradation. In: The Herbicide Glyphosate. Edited by E. Grossbard and D. Atkinson. Butterworths, London.
- Torstensson, N.T.L., L.N. Lundgren, and J. Stenstrom. 1989. Influence of climatic and edaphic factors on persistence of glyphosate and 2,4-D in forest soils.
- U.S. DOI (U.S. Department of the Interior). Bureau of Land Management. 1992.Western Oregon program: Management of competing vegetation. Final record of decision. Oregon State office. August 1992.
- U.S. EPA (U.S. Environmental Protection Agency). 1972. The Pollution Potential in Pesticide Manufacturing, EPA Reprot TS-00-72-04, June 1972.
- U.S. EPA (U.S. Environmental Protection Agency). 1984. Environmental Fates and Impacts of Major Forest Use Pesticides. Office of Pesticides and Toxic Substances.
   Contract No. 68-02-3174. USDA Forest Service Agriculture Handbook #633 Vol. 195. TRW, 1981. Washington, D.C.
- U.S. EPA (U.S. Environmental Protection Agency). 1986a. Pesticides in groundwater: background document. Office of Pesticide Programs and Office of Groundwater Protection. Washington, D.C.

- U.S. EPA (U.S. Environmental Protection Agency). 1986b. Pesticide fact sheet.
   Glyphosate. EPA 540/FS-88-124. Fact Sheet Number 173. U.S. Environmental
   Protection Agency, Office of Pesticide Programs, Washington, D.C. June 1986.
- U.S. EPA (U.S. Environmental Protection Agency). 1987. 2,4-Dichlorophenoxyacetic acid, health advisory. Office of Drinking Water, Washington, D.C.
- U.S. EPA (U.S. Environmental Protection Agency). 1988a. Guidance for the reregistration of pesticide products containing 2,4-dichlorophenoxyacetic acid (2,4-D). EPA 540/RS-88-115. Office of Pesticides and Toxic Substances, Washington, D.C.
- U.S. EPA (U.S. Environmental Protection Agency). 1988b. 2,4-D registration standard: ecological effects topical summaries. Hazard Evaluation Division, Ecological Effects Branch, Washington, D.C.
- U.S. EPA (U.S. Environmental Protection Agency). 1992. Pesticide environmental fate one line summary. Environmental Fate and Effects Division, Washington, D.C.
- U.S.F.S. (U.S. Forest Service). 1988. Managing competing and unwanted vegetation, Final environmental impact statement, Appendices D & H. Pacific Northwest Region, Portland, OR.
- Valent U.S.A. Corporation. 1991. Material safety data sheet for Valent X-77 spreader. Walnut Creek, CA.
- Watkins, C.E., D.D. Thayer, and W.T. Haller. 1985. Toxicity of adjuvants to bluegill. Bull. Environ. Contam. Toxicol. 34:138-142.
- Watson, J.R. 1977. Seasonal variation in the biodegradation of 2,4-D in river water. Water Res. 11:153-157 (as cited in Birmingham and Colman 1985).
- Weber, J.B., P.W. Perry, and R.P. Upchurch. 1965. The influence of temperature and time on the adsorption of paraquat, diquat, 2,4-D, and prometone by clays, charcoal, and an anion-exchange resin. Proc. Soil Sci. Soc. America 29:678-688 (as cited in Hoeppel and Westerdahl 1983).

- Welker, W.V. and D.N. Riemer. 1982. Fragrant waterlily (*Nymphaea odorata*) control with multiple applications of glyphosate. Weed Sci. 30:145-146.
- Westerdahl, H.E. and K.D. Getsinger (eds). 1988. Aquatic plant identification and herbicide use guide. Volume 1: aquatic herbicides and application equipment. Technical report A-88-9. U.S. Army Corps of Engineers, Vicksburg, MI.
- Wilbur-Ellis Company. 1992. Material safety data sheet for R-11 spreader activator. Fresno, CA.
- Wojtalik, T.A., T.F. Hall, and L.O. Hill. 1971. Monitoring ecological conditions associated with wide-scale applications of DMA 2,4-D to aquatic environments. Pestic. Monitor. J. 4:184-203 (as cited in Birmingham and Colman 1985).
- WSDA (Washington State Department of Agriculture). 1992. Guide to pesticides registered in Washington (retrieval from Washington State University database). Retrieval from Washington State University data base, Pullman, WA.
- Zepp, R.G., R.L. Wolfe, J.A. Gordon, and G.L. Baughman. 1975. Dynamics of 2,4-D esters in surface waters. Hydrolysis, photolysis, and vaporization. Environ. Sci. Technol. 9:1144-1149.

# APPENDIX 1 Pesticide Labeling

## SUPPLEMENTAL LABELING

READ AND FOLLOW THE ENTIRE LABEL FOR RODEO® HERBICIDE BEFORE PROCEEDING WITH THE USE DIRECTIONS CONTAINED IN THIS SUPPLEMENTAL LABELING.

"Label" as used in this supplemental labeling refers to the label booklet for Rodeo herbicide and this supplement.

This supplemental label has not been approved for use in California.



(EPA Reg. No. 524-343)

## RODEO HERBICIDE FOR CONTROL OF CORDGRASS (SPARTINA SPP.)

## Keep out of reach of children.

## **CAUTION!**

In case of an emergency involving this product, Call Collect, day or night, (314) 694-4000.

Rodec® is a registered trademark of Monsanto Company.

## **DIRECTIONS FOR USE**

It is a violation of Federal law to use this product in any manner inconsistent with the labeling.

This label must be in the possession of the user at the time of the herbicide application.

## BROADCAST APPLICATIONS (AIR)

Apply 4 to 7-1/2 pints of this product in 10 gallons of spray solution per acre. Aerial applications may be made by helicopter only. Add 1 to 2 quarts of nonionic surfactant per 100 gallons of spray solution.

## BROADCAST APPLICATIONS (GROUND)

Apply 4 to 7-1/2 pints of this product in 10 to 60 gallons of spray solution per acre. For best results, ensure that complete cov-

erage of cordgrass clumps is achieved. Add 1 to 2 quarts of a nonionic surfactant per 100 gallons of spray solution.

## HAND-HELD AND HIGH-VOLUME EQUIPMENT

Apply a 2 to 5 percent solution of this product. Ensure that complete coverage of cordgrass clumps is achieved. Do not spray to the point of run-off. Add 1 to 2 quarts of a nonionic surfactant per 100 gallons of spray solution.

## WIPER APPLICATIONS

For wick or wiper applications, mix 1 gallon if this product with 2 gallons of clean water to make a 33 percent solution. Addition of a nonionic surfactant at a rate of 10 percent by volume of the total herbicide solution is recommended.

In heavy stands, a double application in opposite directions may improve results.

## APPLICATION CONDITIONS

NOTE: Schedule applications in order to allow 6 hours before treated plants are covered by tidewater. Rainfall or immersion within 6 hours after application may reduce effectiveness.

The presence of debris and silt on the cordgrass plants will reduce performance of this product. It may be necessary to wash targeted plants prior to application to improve uptake of this product into the plant.

Read the "LIMIT OF WARRANTY AND LIA-BILITY" in the label booklet for Rodeo before using this product. Those terms apply to this supplemental label and, if those terms are not acceptable, return the product unopened at once.

MAP-3213-4/10/91

© MONSANTO COMPANY 1991

MONSANTO COMPANY AGRICULTURAL PRODUCTS ST LOUIS MISSOURI 53157



This sample label is current as of March 1, 1990. The product descriptions and recommendations provided in this sample label are for background information only. Always refer to the label on the product container before using Monsanto or any other agrichemical product.



Complete Directions for Use in Aquatic and Other Noncrop Sites.

EPA Reg. No. 524-343
AVOID CONTACT WITH FOLIAGE, GREEN STEMS, OR
FRUIT OF CROPS, DESIRABLE PLANTS AND TREES,
SINCE SEVERE INJURY OR DESTRUCTION MAY RESULT.
© RODEO is a registered trademark of Monsanto
Company.

This product has been approved for use in California except as stated otherwise on page 42.

1990-1

892.38-000.88/CG

Read the entire label before using this product.

Use only according to label instructions.

Read "LIMIT OF WARRANTY AND LIABILITY" before buying or using. If terms are not acceptable, return at once unopened.

REFORMULATION IS PROHIBITED. SEE INDIVIDUAL CONTAINER LABEL FOR REPACKAGING LIMITATIONS.

## LIMIT OF WARRANTY AND LIABILITY

This Company warrants that this product conforms to the chemical description on the label and is reasonably fit for the purposes set forth in the Complete Directions for Use label booklet ("Directions") when used in accordance with those Directions under the conditions described therein. NO OTHER EXPRESS WARRANTY OR IMPLIED WARRANTY OF FITNESS FOR PARTICULAR PURPOSE OR MERCHANTABILITY OR ANY OTHER EXPRESS OR IMPLIED WARRANTY IS MADE. This warranty is also subject to the conditions and limitations stated herein.

Buyer and all users shall promptly notify this Company of any claims whether based in contract, negligence, strict liability, other tort or otherwise.

Buyer and all users are responsible for all loss or damage from use or handling which results from conditions beyond the control of this Company, including but not limited to. incompatibility with products other than those set forth in the Directions, application to or contact with desirable vegetation, unusual weather, weather conditions which are outside the range considered normal at the application site and for the time period when the product is applied, as well as weather conditions which are outside the application ranges set forth in the Directions, application in any manner not explicitly set forth in the Directions. moisture conditions outside the moisture range specified in the Directions, or the presence of products other than those set forth in the Directions in or on the soil or treated vegetation.

THE EXCLUSIVE REMEDY OF THE USER OR BUYER, AND THE LIMIT OF THE LIABILITY OF THIS COMPANY OR ANY OTHER SELLER FOR ANY AND ALL LOSSES. INJURIES OR DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT (INCLUDING CLAIMS BASED IN CONTRACT. NEGLIGENCE. STRICT LIABILITY.

OTHER TORT OR OTHERWISE) SHALL BE THE PURCHASE PRICE PAID BY THE USER OR BUYER FOR THE QUANTITY OF THIS PRODUCT INVOLVED, OR, AT THE ELECTION OF THIS COMPANY OR ANY OTHER SELLER. THE REPLACEMENT OF SUCH QUANTITY, OR, IF NOT ACQUIRED BY PURCHASE, REPLACEMENT OF SUCH QUANTITY. IN NO EVENT SHALL THIS COMPANY OR ANY OTHER SELLER BE LIABLE FOR ANY INCIDENTAL. CONSEQUENTIAL, OR SPECIAL DAMAGES.

Buyer and all users are deemed to have accepted the terms of this LIMIT OF WARRANTY AND LIABILITY which may not be varied by any verbal or written agreement.

## PRECAUTIONARY STATEMENTS

## Hazards to Humans and Domestic Animals

Keep out of reach of children. CAUTION!

MAY CAUSE EYE IRRITATION. MAY BE HARMFUL IF INHALED.

Avoid contact with eyes, skin or clothing. Avoid breathing vapors or spray mist.

Wash thoroughly with soap and water after handling. FIRST AID: IF IN EYES, flush with plenty of water for at

least 15 minutes. Get medical attention. IF ON SKIN, flush with water. Wash clothing before

IF INHALED, remove individual to fresh air. Seek medical attention if breathing difficulty develops.

In case of an emergency involving this product, Call Collect, day or night, (314) 694-4000.

## **Environmental Hazards**

Do not contaminate water when disposing of equipment washwaters. Treatment of aquatic weeds can result in oxygen depletion or loss due to decomposition of dead plants. This oxygen loss can cause fish suffocation. In case of:

SPILL or LEAK, soak up and remove to a landfill.

## Physical or Chemical Hazards

Spray solutions of this product should be mixed, stored and applied only in stainless steel, aluminum, fiberglass, plastic and plastic-lined steel containers.

DO NOT MIX, STORE OR APPLY THIS PRODUCT OR SPRAY SOLUTIONS OF THIS PRODUCT IN GALVANIZED STEEL OR UNLINED STEEL (EXCEPT STAINLESS STEEL) CONTAINERS OR SPRAY TANKS. This product or spray solutions of this product react with such containers and tanks to produce hydrogen gas which may form a highly combustible gas mixture. This gas mixture could flash or explode, causing serious personal injury, if ignited by open flame, spark, welder's torch, lighted cigarette or other ignition source.

ACTIVE INGREDIENT:

100.0%

\*Contains 648 grams per litre or 5.4 pounds per U.S. gallon of the active ingredient, glyphosate, in the form of its isopropylamine salt. Equivalent to 480 grams per litre or 4 pounds per U.S. gallon of the acid, glyphosate.

## **DIRECTIONS FOR USE**

It is a violation of Federal law to use this product in any manner inconsistent with its labeling.

## Storage and Disposal

Do not contaminate water, foodstuffs, seed or feed by storage or disposal.

STORAGE:

STORE ABOVE 10°F. (-12°C.) TO KEEP PRODUCT FROM CRYSTALIZING.

Crystals will settle to the bottom. If allowed to crystalize, place in a warm room 68°F. (20°C.) for several days to redissolve and shake well before using.

DISPOSAL

Wastes resulting from the use of this product that cannot be used or chemically reprocessed should be disposed of in a landfill approved for pesticide disposal or in accordance with applicable Federal, state or local procedures.

Emptied container retains vapor and product residue. Observe all labeled safeguards until container is destroyed. Do not reuse container, destroy when empty.

Triple rinse container, then puncture and dispose of in a sanitary landfill, or by incineration, or, if-allowed by state and local authorities, by burning. If burned, stay out of smoke.

## **GENERAL INFORMATION**

This product, a water soluble liquid, mixes readily with water and nonionic surfactant to be applied as a foliar spray for the control or destruction of many herbaceous and woody plants.

This product moves through the plant from the point of foliage contact to and into the root system. Visible effects on most annual weeds occur within 2 to 4 days but on most perennial brush species may not occur for 7 days or more. Extremely cool or cloudy weather following treatment may slow the activity of this product and delay visual effects of control. Visible effects are a gradual wilting and yellowing of the plant which advances to complete browning of above-ground growth and deterioration of underground plant parts.

Unless otherwise directed on this label, delay application until vegetation has emerged and reached the stages described for control of such vegetation under the "Weeds Controlled" section of this label.

Unemerged plants arising from unattached underground rhizomes or root stocks of perennials or brush will not be affected by the spray and will continue to grow. For this reason best control of most perennial weeds or brush is obtained when treatment is made at late growth stages approaching maturity.

Always use the higher rate of this product per acre within the recommended range when vegetation is heavy or dense.

Do not treat weeds or brush under poor growing conditions such as drought stress, disease or insect damage, as reduced control may result. Reduced results may also occur when treating weeds or brush heavily covered with dust.

Reduced control may result when applications are made to any weed or brush species that have been mowed. grazed, or cut, and have not been allowed to regrow to the recommended stage for treatment.

Rainfall or irrigation occurring within 6 hours after application may reduce effectiveness. Heavy rainfall or irrigation within 2 hours after application may wash the product off the foliage and a repeat treatment may be required.

This product does not provide residual weed control. For subsequent residual weed control. follow a label-approved herbicide program. Read and carefully observe the cautionary statements and all other information appearing on the labels of all herbicides used.

Buyer and all users are responsible for all loss or damage in connection with the use or handling of mixtures of this product or other materials that are not expressly recommended in this label. Mixing this product with herbicides or other materials not recommended on this label may result in reduced performance.

#### ATTENTION

AVOID DRIFT. EXTREME CARE MUST BE USED WHEN APPLYING THIS PRODUCT TO PREVENT INJURY TO DESIRABLE PLANTS AND CROPS.

Do not allow the herbicide solution to mist, drip, drift, or splash onto desirable vegetation since minute quantities of this product can cause severe damage or destruction to the crop, plants, or other areas on which treatment was not intended. The likelihood of plant or crop injury occurring from the use of this product is greatest when winds are gusty or in excess of 5 miles per hour or when other conditions, including lesser wind velocities, will allow spray drift to occur. When spraying avoid combinations of pressure and nozzle type that will result in splatter or fine particles (mist) which are likely to drift. AVOID APPLYING AT EXCESSIVE SPEED OR PRESSURE.

NOTE: Use of this product in any manner not consistent with this label may result in injury to persons, animals or crops, or other unintended consequences. When not in use, keep container closed to prevent spills and contamination.

## MIXING AND APPLICATION INSTRUCTIONS

APPLY THESE SPRAY SOLUTIONS IN PROPERLY MAINTAINED AND CALIBRATED EQUIPMENT CAPABLE OF DELIVERING DESIRED VOLUMES. HAND GUN APPLICATIONS SHOULD BE PROPERLY DIRECTED TO AVOID SPRAYING DESIRABLE PLANTS. NOTE: REDUCED RESULTS MAY OCCUR IF WATER CONTAINING SOIL IS USED, such as WATER FROM PONDS AND UNLINED DITCHES.

## **MIXING**

This product mixes readily with water. Mix spray solutions of this product as follows: fill the mixing or spray tank with the required amount of water while adding the required amount of this product (see "Directions for Use" and "Weeds Controlled" sections of this label). Near the end of the filling process, add the required surfactant

and mix well. Remove hose from tank immediately after filling to avoid siphoning back into the water source. During mixing and application, foaming of the spray solution may occur. To prevent or minimize foam, avoid the use of mechanical agitators, place the filling hose below the surface of the spray solution, terminate by-pass and return lines at the bottom of the tank and if needed use an approved anti-foam or defoaming agent.

Keep by-pass line on or near bottom of tank to minimize foaming. Screen size in nozzle or line strainers should be no finer than 50 mesh. Carefully select correct nozzle to avoid spraying a fine mist. For best results with conventional ground application equipment, use flat fan nozzles. Check for even distribution of spray droplets.

When using this product, mix 2 or more quarts of a nonionic surfactant per 100 gallons of spray solution. Use a nonionic surfactant labeled for use with herbicides. The surfactant must contain 50 percent or more active ingredient.

Always read and follow the manufacturer's surfactant label recommendations for best results.

These surfactants should not be used in excess of  $1\ quart$  per acre when making **broadcast** applications.

Clean sprayer and parts immediately after using this product by thoroughly flushing with water and dispose of rinsate according to labeled use or disposal instructions.

Carefully observe all cautionary statements and other information appearing on the surfactant label.

## APPLICATION EQUIPMENT AND TECHNIQUES

## AERIAL EQUIPMENT

See the supplemental label for use of this product by air in California.

Use the recommended rates of this product and surfactant in 3 to 20 gallons of water per acre as a broadcast spray, unless otherwise specified. See the "Weeds Controlled" section of this label for specific rates. Aerial applications of this product may only be made as specifically recommended on this label.

AVOID DRIFT — DO NOT APPLY DURING INVERSION CONDITIONS. WHEN WINDS ARE GUSTY. OR UNDER ANY OTHER CONDITION WHICH WILL ALLOW DRIFT. DRIFT MAY CAUSE DAMAGE TO ANY VEGETATION CONTACTED TO WHICH TREATMENT IS NOT INTENDED. TO PREVENT INJURY TO ADJACENT DESIRABLE VEGETATION. APPROPRIATE BUFFER ZONES MUST BE MAINTAINED.

Coarse sprays are less likely to drift; therefore, do not use nozzles or nozzle configurations which dispense spray as fine spray droplets. Do not angle nozzles forward into the airstream and do not increase spray volume by increasing nozzle pressure.

Drift control additives may be used. When a drift control additive is used, read and carefully observe the cautionary statements and all other information appearing on the additive label.

Ensure uniform application — To avoid streaked, uneven or overlapped application, use appropriate marking devices.

Thoroughly wash aircraft, especially landing gear, after each day of spraying to remove residues of this product accumulated during spraying or from spills. PROLONGED EXPOSURE OF THIS PRODUCT TO UNCOATED STEEL SURFACES MAY RESULT IN CORROSION AND POSSIBLE

FAILURE OF THE PART. LANDING GEAR ARE MOST SUS-CEPTIBLE. The maintenance of an organic coating (paint) which meets aerospace specification MIL-C-38413 may prevent corrosion.

## BOOM EQUIPMENT

For control of weed or brush species listed on this label using conventional boom equipment — Use the recommended rates of this product and surfactant in 3 to 30 gallons of water per acre as a broadcast spray. unless otherwise specified. See the "Weeds Controlled" section of this label for specific rates. As density of vegetation increases, spray volume should be increased within the recommended range to insure complete coverage. Carefully select correct nozzle to avoid spraying a fine mist.

For best results with ground application equipment, use flat fan nozzles. Check for even distribution of spray droplets.

## HAND-HELD and HIGH-VOLUME EQUIPMENT

Use Coarse Sprays Only

For control of weeds listed on this label using knapsack sprayers or high-volume spraying equipment utilizing handguns or other suitable nozzle arrangements — Prepare a ¾ to 1½ percent solution of this product in water, add a nonionic surfactant and apply to foliage of vegetation to be controlled. For specific rates of application and instructions for control of various annual and perennial weeds. see the "Weeds Controlled" section of this label.

Applications should be made on a spray-to-wet basis. Spray coverage should be uniform and complete. Do not spray to point of runoff.

Where less than complete coverage occurs with spot treatments, use a 5 percent spray solution.

Prepare the desired volume of spray solution by mixing the amount of this product in water, shown in the following table:

#### Spray Solution

DESIRED		AMOU	NT OF R	ODEO2	
VOLUME	3,4 0	1%	11,50		5%
1 gallon 25 gallons 100 gallons 2 tablespoor	3 qt.	l qt. l gal.	1% oz. 1% qt. 1% gal.	11	623 OZ.

For use in knapsack sprayers, it is suggested that the recommended amount of this product be mixed with water in a larger container. Fill sprayer with the mixed solution and add the correct amount of surfactant.

## **WEEDS CONTROLLED**

## ANNUAL WEEDS

Apply to actively growing annual grasses and broadleaf weeds.

Allow at least 3 days after application before disturbing treated vegetation. After this period the weeds may be mowed, tilled or burned. See "Directions for Use." "General Information." and "Mixing and Application Instructions" for labeled uses and specific application instructions.

**Broadcast Application** — Use  $1\frac{1}{2}$  pints of this product per acre plus 2 or more quarts of a nonionic surfactant per 100 gallons of spray solution if weeds are less than 6 inches tall. If weeds are greater than 6 inches tall. use  $2\frac{1}{2}$  pints of this product per acre plus 2 or more quarts

of an approved nonionic surfactant per 100 gallons of spray solution.

Hand-Held High-Volume Application — Use a 3/4 percent solution of this product in water plus 2 or more quarts of a nonionic surfactant per 100 gallons of spray solution and apply to foliage of vegetation to be controlled.

When applied as directed under the conditions described in this label, this product plus nonionic surfactant WILL CONTROL the following ANNUAL WEEDS:

Balsamapple<sup>±∞</sup> Momordica charantia

Barley Hordeum vulgare

Barnyardgrass Echinochloa crus-galli Bassia, fivehook

Bassia hyssopifolia

Bluegrass, annual Poa annua

Bluegrass, bulbous Poa bulbosa

Bromus spp.

Buttercup Ranunculus spp.

Bromus secalinus

Chickweed, mouseear Cerastium vulgatum

Cockiebur Xanthium strumarium

Corn, volunteer Zea mays

Crabgrass

Digitaria spp. Dwarfdandelion

Krigia cespitosa Falseflax, smallseed

Camelina microcarpa

Fiddleneck Amsinckia spp.

Flaxleaf fleabane Conyza bonariensis

Fleshane

Erigeron spp. Foxtail

Setaria spp. Foxtail, Carolina

Alopecurus carolinianus Spanishneedles\*

Groundsel, common Senecio vulgaris

Horseweed/Marestail Conyza canadensis

Kochia

Kochia scoparia

Lambsquarters, common Chenopodium album

Lettuce, prickly Lactuca serriola

Morningglory Ipomoea spp. Mustard, tansv Descurainia pinnata

Mustard, tumble Sisymbrium altissimum

Mustard, wild Sinapis arvensis Oats, wild

**Panicum** Panicum spp. Pennycress, field

Avena fatua

Thlaspi arvense Pigweed, redroot

Pigweed, smooth Amaranthus hybridus

Amaranthus retroflexus

Ragweed, common Ambrosia artemisiifolia

Ragweed, giant Ambrosia trifida

Rocket, London Sisymbrium irio

Rye

Secale cereale

Ryegrass, Italian® Lolium multiflorum

Sandbur, field Cenchrus spp.

Shattercane Sorghum bicolor

Shepherdspurse

Capsella bursa-pastoris

Signalgrass, broadleaf Brachiaria platyphylla

Smartweed, Pennsylvania Polygonum pensylvanicum

Sowthistle, annual Sonchus oleraceus

Bidens bipinnata

Stinkgrass

Eragrostis cilianensis Sunflower

Helianthus annuus Thistle, Russian

Salsola kali Spurry, umbrella Holosteum umbellatum

Velvetleaf Abutilon theophrasti

Wheat

Triticum aestivum

Mustard, blue Chorispora tenella Witchgrass Panicum capillare

\*Apply 3 pints of this product per acre. \*\*Apply with hand-held equipment only.

Annual weeds will generally continue to germinate from seed throughout the growing season. Repeat treatments will be necessary to control later germinating weeds.

#### PERENNIAL WEEDS

Apply this product as follows to control or destroy most vigorously growing perennial weeds. Unless otherwise directed, allow at least 7 days after application before disturbing vegetation.

Add 2 or more quarts of a nonionic surfactant per 100 gallons of spray solution to the rates of this product given in this list. See the "General Information," "Directions for Use," and "Mixing and Application" sections of this label for specific uses and application instructions.

NOTE: If weeds have been moved or tilled, do not treat until regrowth has reached the recommended stages. Fall treatments must be applied before a killing frost.

Repeat treatments may be necessary to control weeds regenerating from underground parts or seed.

When applied as recommended under the conditions described, this product plus surfactant WILL CONTROL the following PERENNIAL WEEDS:

Alfalfa Medicago sativa

Alligatorweed\* Alternanthera philoxeroides

Artichoke, Jerusalem Helianthus tuberosus

Bahiagrass Paspalum notatum

Bermudagrass Cynodon dactylon

Bindweed, field Convolvulus arvensis

Bluegrass, Kentucky Poa pratensis

Blueweed, Texas Helianthus ciliaris

Brackenfern Pteridium spp.

Bromegrass, smooth Bromus inermis

Canarygrass, reed Phalaris arundinacea

Cattail Typha spp.

Clover, red Trifolium pratense

Clover, white Trifolium repens

Cogongrass Imperata clylindrica

Cutgrass, giant™ Zizaniopsis miliacea

**Dallisgrass** Paspalum dilatatum

**Dandelion** Taraxacum officinale Lantana Lantana camara

Loosestrife, purple Lythrum salicaria

Lotus, American Nelumbo lutea

Maidencane Panicum hematomon

Milkweed Asclepias spp.

Muhly, wirestem Muhlenbergia frondosa

Mullein, common Verbascum thapsus

Napiergrass Pennisetum purpureum

Nightshade, silverleaf Solanum elaeagnifolium

Nutsedge: purple, yellow Cyperus rotundus Cyperus esculentus

Orchardgrass Dactylis glomerata

**Pampasgrass** Cortaderia jubata

Paragrass Brachiaria mutica

Phragmites\*\* Phragmites spp.

Quackgrass Agropyron repens

Reed, giant Arundo donax Ryegrass, perennial

Lolium perenne Smartweed, swamp

Polygonum coccineum

Dock, curly Rumex crispus

Fescue, tall

Spatterdock Nuphar luteum

Sweet potato, wild\* Dogbane, hemp Apocynum cannabinum Ipomoea pandurata

Timothy

**Fescue** Thistle Festuca spp. Cirsium arvense

Phleum pratense Guineagrass Torpedograss\* Panicum maximum

Horsenettle . Solanum carolinense Horseradish

Festuca arundinacea

Armoracia rusticana **Johnsongrass** 

Sorghum halepense Kikuyugrass Pennisetum clandestinum

Knapweed Centaurea repens

Panicum repens Tules, common Scirpus acutus

Vaseygrass

Paspalum urvillei Waterhyacinth Eichornia crassipes

Waterlettuce Pistia stratiotes

Waterprimrose Ludwigia spp. Wheatgrass, western

Agropyron smithii

"Partial control.

\*\*Partial control in southeastern states. See specific recommendations below.

Alligatorweed - Apply 6 pints of this product per acre as a broadcast spray or as a 114 percent solution with hand-held equipment to provide partial control of alligatorweed. Apply when most of the target plants are in bloom. Repeat applications will be required to maintain such control.

Bermudagrass - Apply 712 pints of this product per acre as a broadcast spray or as a 112 percent solution with hand-held equipment. Apply when target plants are actively growing and when seed heads appear.

Bindweed, field/Silverleaf Nightshade/Texas Blueweed - Apply 6 to 71/2 pints of this product per acre as a broadcast spray west of the Mississippi River and 412 to 6 pints of this product per acre east of the Mississippi River. With hand-held equipment, use a 1½ percent solution. Apply when target plants are actively growing and are at or beyond full bloom. For silverledf nightshade, best results can be obtained when application is made after berries are formed. Do not treat when weeds are under drought stress. New leaf development indicates active growth. For best results apply in late summer or fall.

Brackenfern - Apply 4½ to 6 pints of this product per acre as a broadcast spray or as a 34 to 1 percent solution with hand-held equipment. Apply to fully expanded fronds which are at least 18 inches long.

Cattail - Apply 41/2 to 6 pints of this product per acre as a broadcast spray or as a 34 percent solution with hand-held equipment. Apply when target plants are actively growing and are at or beyond the early-to-full bloom stage of growth. Best results are achieved when application is made during the summer or fall months.

Cogongrass - Apply 4.5 to 7.5 pints of this product per acre as a broadcast spray. Apply when cogongrass is at least 18 inches tall and actively growing in late summer or fall. Allow 7 or more days after application before tillage or mowing. Due to uneven stages of growth and the dense nature of vegetation preventing good spray coverage, repeat treatments may be necessary to maintain control.

cutgrass, giant — Apply 6 pints of this product per acre as a broadcast spray or as a 1 percent solution with and-held equipment to provide partial control of giant stgrass. Repeat applications will be required to maintain such control especially where vegetation is partially submerged in water. Allow for substantial egrowth to the seven-to-ten-leaf stage prior to extreatment.

Dogbane, hemp/Knapweed/Horseradish — Apply 6 nints of this product per acre as a broadcast spray or :s a 1½ percent solution with hand-held equipment. Apply when target plants are actively growing and most have reached the late bud-to-flower stage of growth. For best results, apply in late summer or fall.

iascue, tall — Apply 4½ pints of this product per acre as a broadcast spray or as a 1 percent solution with hand-held equipment. Apply when target plants are actively growing and most have reached the boot-to-nead stage of growth. When applied prior to the boot stage, less desirable control may be obtained.

Guineagrass — Apply 4½ pints of this product per acre is a broadcast spray or as a 34 percent solution with nand-held equipment. Apply when target plants are actively growing and when most have reached at least the 7-leaf stage of growth.

Johnsongrass / Bluegrass, Kentucky / Bromegrass, smooth / Canarygrass, reed / Orchardgrass / Ryegrass, perennial / Timothy / Wheatgrass, western — Apply 3 to 4½ pints of this product per acre as a broadcast spray or as a ¾ percent solution with hand-held equipment. Apply when target plants are actively growing and most have reached the boot-to-head stage of growth. When applied prior to the boot stage, less desirable control may be obtained. In the fall, apply before plants have turned brown.

Lantana — Apply this product as a 34 to 1 percent solution with hand-held equipment. Apply to actively growing lantana at or beyond the bloom stage of growth. Use the higher application rate for plants that have reached the woody stage of growth.

Loosestrife, purple — Apply 4 pints of this product per acre as a broadcast spray or as a 1 percent solution using hand-held equipment. Treat when plants are actively growing at or beyond the bloom stage of growth. Best results are achieved when application is made during summer or fall months. Fall treatments must be applied before a killing frost.

Lotus, American — Apply 4 pints of this product per acre as a broadcast spray or as a 34 percent solution with hand-held equipment. Treat when plants are actively growing at or beyond the bloom stage of growth. Best results are achieved when application is made during summer or fall months. Fall treatments must be applied before a killing frost. Repeat treatment may be necessary to control regrowth from underground parts and seeds.

Maidencane / Paragrass — Apply 6 pints of this product per acre as a broadcast spray or as a ¾ percent solution with hand-held equipment. Repeat treatments will be required, especially to vegetation partially submerged in water. Under these conditions, allow for regrowth to the seven-to-ten leaf stage prior to retreatment.

**Milkweed, common** — Apply  $4\frac{1}{2}$  pints of this product per acre as a broadcast spray or as a  $1\frac{1}{2}$  percent solution with hand-held equipment. Apply when target plants are actively growing and most have reached the late bud-to-flower stage of growth.

Nutsedge, purple, yellow — Apply 4½ pints of this product per acre as a broadcast spray, or as a ¾ percent solution with hand-held equipment to control existing nutsedge plants and immature nutlets attached to treated plants. Apply when target plants are in flower or when new nutlets can be found at rhizome tips. Nutlets which have not germinated will not be controlled and may germinate following treatment. Repeat treatments will be required for long-term control.

Pampasgrass — Apply a 1.5 percent solution of this product with hand-held equipment when plants are actively growing.

Phragmites — For partial control of phragmites in Florida and the counties of other states bordering the Gulf of Mexico, apply 7.5 pints per acre as a broadcast spray or apply a 1½ percent solution with hand-held equipment. In other areas of the U.S., apply 4 to 6 pints per acre as a broadcast spray or apply a ¾ percent solution with hand-held equipment for partial control. For best results, treat during late summer of fall months when plants are actively growing and in full bloom. Due to the dense nature of the vegetation, which may prevent good spray coverage and uneven stages of growth, repeat treatments may be necessary to maintain control. Visual control symptoms will be slow to develop.

Quackgrass / Kikuyugrass / Muhly, wirestem — Apply 3 to 4½ pints of this product per acre as a broadcast spray or as a ¾ percent solution with hand-held equipment when most quackgrass or wirestem muhly is at least 8 inches in height (3- or 4-leaf stage of growth) and actively growing. Allow 3 or more days after application before tillage.

Reed, giant — For control of giant reed, apply a 1.5 percent solution of this product with hand-held equipment when plants are actively growing. Best results are obtained when applications are made in late summer to fall.

Spatterdock — Apply 6 pints of this product per acre as a broadcast spray or as a 34 percent solution with handheld equipment. Apply when most plants are in full bloom. For best results, apply during the summer or fall months.

Sweet potato, wild — Apply this product as a 1½ percent solution using hand-held equipment. Apply to actively growing weeds that are at or beyond the bloom stage of growth. Repeat applications will be required. Allow the plant to reach the recommended stage of growth before retreatment.

Thistle — Apply 3 to  $4\frac{1}{2}$  pints of this product per acre as a broadcast spray or as a  $1\frac{1}{2}$  percent solution with hand-held equipment. Apply when target plants are actively growing and are at or beyond the bud stage of growth.

Torpedograss — Apply 6 to 7½ pints of this product per acre as a broadcast spray or as a ¾ to 1½ percent solution with hand-held equipment to provide partial control of torpedograss. Use the lower rates under terrestrial conditions, and the higher rates under partially submerged or a floating mat condition. Repeat treatments will be required to maintain such control.

Tules, common — Apply this product as a 1½ percent solution with hand-held equipment. Apply to actively growing plants at or beyond the seedhead stage of growth. After application visual symptoms will be slow to appear and may not occur for 3 or more weeks.

Waterhyacinth — Apply 5 to 6 pints of this product per acre as a broadcast spray or apply a 34 to 1 percent so-

lution with hand-held equipment. Apply when target plants are actively growing and at or beyond the early bloom stage of growth. After application, visual symptoms may require 3 or more weeks to appear with complete necrosis and decomposition usually occurring within 60 to 90 days. Use the higher rates when more rapid visual effects are desired.

Waterlettuce — For control, apply a 34 to 1 percent solution of this product with hand-held equipment to actively growing plants. Use higher rates where infestations are heavy. Best results are obtained from mid-summer through winter applications. Spring applications may require retreatment.

Waterprimrose — Apply this product as a % percent solution using hand-held equipment. Apply to plants that are actively growing at or beyond the bloom stage of growth, but before fall color changes occur. Thorough coverage is necessary for best control.

Other perennials listed on this label — Apply  $4\frac{1}{2}$  to  $7\frac{1}{2}$  pints of this product per acre as a broadcast spray or as a  $\frac{3}{2}$  to  $1\frac{1}{2}$  percent solution with hand-held equipment. Apply when target plants are actively growing and most have reached early head or early bud stage of growth.

#### **WOODY BRUSH AND TREES**

When applied as recommended under the conditions described, this product plus surfactant CONTROLS or PARTIALLY CONTROLS the following woody brush plants and trees:

plants and trees:	
Alder	Maple:
Alnus spp.	Red™≠
Ash**	Acer rubrum
Fraxinus spp.	Sugar
Aspen, quaking	Acer saccharum
Populus tremuloides	Vine"
Bearmat, Bearclover	Acer circinatum
Chamaebatia foliolosa	Monkey Flower*
Birch	Mimulus guttatus
Betula spp.	Oak:

Rubus spp.	Quercus velutina
Broom:	Northern pine
French	Quercus palustris
Cytisus	Pnet

Blackberry

Black\*

•	
monspessulanus	Quercus stellat
Scotch	Red
Cytisus scoparius	Quercus rubra

.,	£
Buckwheat, California™	Southern red
Eriogonum fasciculatum	Quercus falcata
Cascara <sup>±</sup>	White*

Rhamnus purshiana	Quercus alba
Catsclaw* Acacia greggi	Persimmon* Diospyros spp.
Ceanothus Spp.	Poison lvy Rhus radicans
Chamise Adenostoma fasciculatum	Poison Oak Rhus toxicodendron
Cherry:	Poplar, yellow* Liriodendron tulipifera

Bitter	
Prunus emarginata	Raspberry
Black	Rubus spp.
Prunus serotina	Rose, multiflora
	Rosa multiflora

Pin Prunus pensylvanica Coyote brush

Baccharis consanguinea Elaeagnus angustifolia

Creeper, Virginia\* **Parthenocissus** 

auinauefolia Dewberry Rubus trivialis

Elderberry Sambucus spp.

Ulmus spp. Eucalyptus, bluegum

Eucalyptus globulus Hasardia\*

Hawthorn

Crataegus spp. Hazel Corylus spp.

Holly, Florida; Brazilian Peppertree

Schinus

terebinthifolius

Honeysuckie Lonicera spp. Kudzu

Pueraria lobata Locust, black\*

Robinia pseudoacacia Manzanita

Arctostaphylos spp.

Russian-olive

Sage, black Saliva mellifera

Sagebrush, California Artemisia californica

Salmonberry Rubus spectabilis

Saltbush, Sea myrtle Baccaharis halimifolia

Sassafras

Sassafrass aibidum Sourwood\*

Oxydendrum arboreum

Haplopappus squamosus Sumac: Poison\*

> Rhus vernix Smooth<sup>a</sup> Rhus glabra

Winged\* Rhus copallina

Sweet gum

Liquidambar styraciflua

Swordfern\*

Polystichum munitum

Tallowtree, Chinese Sapium sebiferum

Thimbleberry Rubus parvifiorus

Tobacco, tree\* Nicotiana glauca Trumpetcreeper

Campsis radicans Waxmyrtle, southern\* Myrica cerifera

Willow Salix spp.

\*Partial control

\*\*See below for control or partial control instructions. NOTE: If brush has been moved or tilled or trees have been cut, do not treat until regrowth has reached the recommended stage of growth.

Apply the recommended rate of this product plus 2 or more quarts of a nonionic surfactant per 100 gallons of spray solution when plants are actively growing and unless otherwise directed, after full-leaf expansion. Use the higher rate for larger plants and or dense areas of growth. On vines, use the higher rate for plants that have reached the woody stage of growth. Best results are obtained when application is made in late summer or fall after fruit formation.

In arid areas, best results are obtained when application is made in the spring to early summer when brush species are at high moisture content and are flowering. Ensure thorough coverage when using hand-held equipment. Symptoms may not appear prior to frost or senescence with fall treatments.

Allow 7 or more days after application before tillage. mowing or removal. Repeat treatments may be necessary to control plants regenerating from underground parts or seed. Some autumn colors on undesirable deciduous species are acceptable provided no major leaf drop has occurred. Reduced performance may result if fall treatments are made following a frost.

See "Directions for Use" and "Mixing and Application Instructions" section of this label for labeled use and specific application instructions.

Apply the product as follows to control or partially control the following woody brush and trees.

Alder / Blackberry / Dewberry / Honeysuckle / Oak, Post / Raspberry — For control, apply 4½ to 6 pints per acre as a broadcast spray or as a ¾ to 1¼ percent solution with hand-held equipment.

Aspen, Quaking/Hawthorn/Trumpetcreeper - For control, apply 3 to 4½ pints of this product per acre as a broadcast spray or as a % to 1% percent solution with hand-held equipment.

Birch / Elderberry / Hazel / Salmonberry / Thimbleberry - For control, apply 3 pints per acre of this product as a broadcast spray or as a ¾ percent solution with hand-held equipment.

Broom: French, Scotch — For control, apply a 11/4 to 11/2 percent solution with hand-held equipment.

Buckwheat, California/Hasardia/Monkey Flower/ Tobacco, Tree - For partial control of these species. apply a 34 to 11/2 percent solution of this product as a foliar spray with hand-held equipment. Thorough coverage of foliage is necessary for best results.

Catsclaw - For partial control, apply a 11/4 to 11/2 percent solution with hand-held equipment and at least 50 percent of the new leaves are fully developed.

Cherry: Bitter, Black, Pin/Oak, Southern Red/Sweet Gum — For control, apply 3 to 7½ pints of this product per acre as a broadcast spray or as a 1 to 1½ percent solution with hand-held equipment.

Coyote Brush — For control, apply a 1¼ to 1½ percent solution with hand-held equipment when at least 50 percent of the new leaves are fully developed.

Eucalyptus, bluegum - For control of eucalyptus resprouts, apply a 112 percent solution of this product with hand-held equipment when resprouts are 6 to 12 feet tall. Ensure complete coverage. Apply when plants are actively growing. Avoid application to droughtstressed plants. For control of eucalyptus trees 2 to 24 inches in diameter, cut trees as close to the soil surface as desired. Apply a 50 to 100 percent solution of this product to freshly cut surface immediately after cutting. Delay in applying this product may result in poor performance.

Holly, Florida / Waxmyrtle — For partial control, apply this product as a 1½ percent solution with hand-held equipment.

Kudzu — For control, apply 6 pints of this material per acre as a broadcast spray or as a 1½ percent solution with hand-held equipment. Repeat applications will be required to maintain control.

Maple, Red\*\* - For control, apply as a ¾ to 1¼ percent solution with hand-held equipment when leaves are fully developed. For partial control, apply 2 to 7%pints of this product per acre as a broadcast spray.

Maple, Sugar / Oak: Northern Pin, Red — For control, apply as a ¾ to 1¼ percent solution with hand-held equipment when at least 50 percent of the new leaves are fully developed.

Poison Ivy / Poison Oak — For control, apply 6 to 71/2 pints of this product per acre as a broadcast spray or as a  $1\frac{1}{2}$  percent solution with hand-held equipment. Repeat applications may be required to maintain control. Fall treatments must be applied before leaves lose green color.

Rose, Multiflora - For control, apply 3 pints of this product per acre as a broadcast spray or as a 34 percent solution with hand-held equipment. Treatments should be made prior to leaf deterioration by leaffeeding insects.

Sage, Black/Sagebrush, California/Chamise/ Tallowtree, Chinese - For control of these species. apply a 3/4 percent solution of this product as a foliar spray with hand-held equipment. Thorough coverage of foliage is necessary for best results.

Saltbush, Sea myrtle — For control, apply this product as a 1 percent solution with hand-held equipment.

Willow - For control, apply 4½ pints of this product per acre as a broadcast spray or as a 3/4 percent solution with hand-held equipment.

\*Other woody brush and trees listed in this label -For partial control, apply 3 to 7½ pints of this product per acre as a broadcast spray or as a 34 to 112 percent solution with hand-held equipment.

## AOUATIC AND OTHER NONCROP SITES

When applied as directed and under the conditions described in the "Weeds Controlled" section of this label, this product will control or partially control the labeled weeds growing in the following industrial. recreational, and public areas or other similar sites.

Aquatic Sites - This product may be applied to emerged weeds in all bodies of fresh and brackish water which may be flowing, nonflowing, or transient. This includes lakes, rivers, streams, ponds, estuaries, rice levees, seeps, irrigation and drainage ditches. canals, reservoirs, and similar sites.

If aquatic sites are present in the noncrop area and are part of the intended treatment, read and observe the following directions:

There is no restriction on the use of treated water for irrigation, recreation, or domestic purposes.

Consult local state fish and game agency and water control authorities before applying this product to public water. Permits may be required to treat such water. NOTE: Do not apply this product within 12 mile upstream of a potable water intake in flowing water (i.e., river, stream, etc.) or within  $\frac{1}{2}$  mile of a potable water intake in a standing body of water such as lake, pond, or reservoir.

This product does not control plants which are completely submerged or have a majority of their foliage under water.

For treatments after drawdown of water or in dry ditches, allow 7 or more days after treatment before reintroduction of water. Apply this product within one day after drawdown to ensure application to actively

Floating mats of vegetation may require retreatment. Avoid wash-off of sprayed foliage by spray boat or recreational boat backwash or by rainfall within 6 hours of application. Do not retreat within 24 hours following the initial treatment.

Applications made to moving bodies of water must be made while traveling upstream to prevent concentration of this herbicide in water. When making any bankside applications, do not overlap more than 1 foot into open water. Do not spray across open moving bodies of water, or where weeds do not exist. The maxi-

num application rate of 7½ pints per acre must not be exceeded in any single application.

When emerged infestations require treatment of the otal surface area of impounded water, treating the area n strips may avoid oxygen depletion due to decaying vegetation. Oxygen depletion may result in fish kill.

## Other Noncrop-Type Sites:

Airports **Golf Courses** Highways & Roadsides

Pipeline. Power, Telephone & Utility Rights of Way

Industrial Plant Sites umberyards

Pumping Installations Railroads

Parking Areas Parks

Schools Storage Areas Similar Sites

Petroleum Tank Farms

## INJECTION AND FRILL APPLICATIONS

Noody vegetation may be controlled by injection or frill application of this product. Apply this product using suitable equipment which must penetrate into living issue. Apply the equivalent of 1 ml of this product per 2 to 3 inches of trunk diameter. This is best achieved by applying 25 to 100 percent concentration of this material either to a continuous frill around the tree or as cuts evenly spaced around the tree below all branches. As tree fiameter increases in size, better results are achieved by applying dilute material to a continuous frill or more closely spaced cuttings. Avoid application techniques hat allow runoff to occur from frill or cut areas in species that exude sap freely after frills or cutting. In species such as these, make frill or cut at an oblique angle so as to produce a cupping effect and use undiluted material. For best results, applications should be nade during periods of active growth and full leaf expansion.

This treatment WILL CONTROL the following woody pecies:

Oak Ouercus spp.

Sweet gum Liquidambar styraciflua

Poplar Populus spp.

Sycamore Platanus

occidentalis

his treatment WILL SUPPRESS the following woody species:

Black gum Nyssa sylvatica - Hickory Carya spp.

Dogwood Cornus spp. Maple, red Acer rubrum

## **CUT STUMP APPLICATION**

. Voody vegetation may be controlled by treating freshly cut stumps of trees and resprouts with this product. Apply this product using suitable equipment to ensure coverage of the entire cambium. Cut vegetation close to the soil surface. Apply a 50 to 100 percent solution of this product to freshly cut surface immediately after cutting. Delay in applying this product may result in educed performance. For best results, trees should be cut during periods of active growth and full leaf expansion

When used according to directions for injection or cut tump application, this product will CONTROL, PARTIAL-LY CONTROL or SUPPRESS most woody brush and tree species, some of which are listed below:

Alder Alnus spp.

Oak

Quercus spp.

Coyotebrush

Poplar Baccharis consanguinea Populus spp.

Dogwood Cornus spp. Salt cedar Tamarix spp.

Eucalyptus, bluegum Eucalyptus glotulus Sweet gum Liquidambar styraciflua

Hickory Carya spp.

Sycamore

Madrone

Platanus occidentalis Tan oak

Arbutus menziesii

Lithocarpus densiflorus

Maple Acer spp. Willow Salix spp.

#### **RELEASE OF BERMUDAGRASS** OR BAHIAGRASS ON **NONCROP SITES**

#### **RELEASE OF DORMANT BERMUDAGRASS AND BAHIAGRASS**

When applied as directed, this product will provide control or suppression of many winter annual weeds and tall fescue for effective release of dormant bermudagrass or bahiagrass. Make applications to dormant bermudagrass or bahiagrass.

For best results on winter annuals, treat when weeds are in an early growth stage (below 6 inches in height) after most have germinated. For best results on tall fescue. treat when fescue is in or beyond the 4 to 6-leaf stage.

#### **WEEDS CONTROLLED**

Rate recommendations for control or suppression of winter annuals and tall fescue are listed below.

Apply the recommended rates of this product in 10 to 25 gallons of water per acre plus 2 quarts nonionic surfactant per 100 gallons of total spray volume.

## WEEDS CONTROLLED OR SUPPRESSED\*

PARENE FLHIR OZ / ACDE

NOTE: C = Control

S = Suppression

	KODEOS		FLUID OZ / AC			CRE
WEED SPECIES	6	9	12	18	24	48
Barley, little	S	С	С	Ç	С	С
Hordeum pusillum						
Bedstraw, catchweed	S	С	С	С	C	С
Galium aparine						
Bluegrass, annual	S	С	С	С	C	C
Poa annua						
Chervil	S	С	С	С	С	C
Chaerophyllum tainturier						
Chickweed, common	S	С	С	C	C	С
Stellaria media						
Clover, crimson	•	S	S	С	С	С
Trifolium incarnatum						
Clover, large hop	•	S	S	С	C	С
Trifolium campestre						
Speedwell, corn	S	С	С	С	С	C
Veronica arvensis						
Fescue, tall	•	٠	•	•	S	S
Festuca arundinacea						
Geranium, Carolina	•	•	S	S	С	С
Geranium carolinianum						
Henbit	•	S	С	С	С	Ç
Lamium amplexicaule						
Ryegrass, Italian	•	•	S	С	С	С
Lolium multiflorum						

	ROD	FLUID OZ / AC			ACRI	
WEED SPECIES	- 6	9	12	18	24	48
Vetch, common	•	•	S	С	С	C
Vicia sativa .						

<sup>\*</sup>These rates apply only to sites where an established competitive turf is present.

## **RELEASE OF ACTIVELY GROWING BERMUDAGRASS**

NOTE: USE ONLY ON SITES WHERE BAHIAGRASS OR BERMUDAGRASS ARE DESIRED FOR GROUND COVER AND SOME TEMPORARY INJURY OR YELLOWING OF THE GRASSES CAN BE TOLERATED.

When applied as directed, this product will aid in the release of bermudagrass by providing control of annual species listed in the "Weeds Controlled" section of this label, and suppression or partial control of certain perennial weeds.

For control or suppression of those annual species listed on this label, use ¾ to 2¼ pints of this product as a broadcast spray in 10 to 25 gallons of spray solution per acre, plus 2 quarts of a nonionic surfactant per 100 gallons of total spray volume. Use the lower rate when treating annual weeds below 6 inches in height (or length of runner in annual vines). Use higher rate as size of plants increases or as they approach flower or seedhead formation.

Use the higher rate for partial control or longer term suppression of the following perennial species. Use lower rates for shorter-term suppression of growth.

Bahiagrass Dallisgrass Fescue (tall) Johnsongrass"= Trumpetcreeper" Vaseygrass

Use only on well-established bermudagrass. Bermudagrass injury may result from the treatment but regrowth will occur under moist conditions. Repeat applications in the same season are not recommended, since severe injury may result.

### BAHIAGRASS SEEDHEAD AND VEGETATIVE SUPPRESSION

When applied as directed in the "Noncrop Sites" section of this label, this product will provide significant inhibition of seedhead emergence and will suppress vegetative growth for a period of approximately 45 days with single applications and approximately 120 days with sequential applications.

Apply this product 1 to 2 weeks after full green-up of bahiagrass or after the bahiagrass has been mowed to a uniform height of 3 to 4 inches. Applications must be made prior to seedhead emergence. Apply 5 fluid ounces per acre of this product, plus 2 quarts of an approved nonionic surfactant per 100 gallons of total spray volume in 10 to 25 gallons of water per acre.

Sequential applications of this product plus nonionic surfactant may be made at approximately 45-day intervals to extend the period of seedhead and vegetative growth suppression. For continued vegetative growth suppression, sequential applications must be made prior to seedhead emergence.

Apply no more than 2 sequential applications per year. As a first sequential application, apply 3 fluid ounces of this product per acre plus nonionic surfactant. A

<sup>\*</sup>Suppression at the higher rate only.

<sup>\*\*</sup>Johnsongrass is controlled at the higher rate.

second sequential application of 2 to 3 fluid ounces per acre plus nonionic surfactant may be made approximately 45 days after the last application.

### CALIFORNIA

This product has been approved by the U.S. Environmental Protection Agency for the uses, crops and sites listed in this label and by California. Approval of the items listed below is pending under the state of California registration requirements. With the exceptions of these items, this booklet contains the material approved by California in label 1990-1.

These use conditions, crops, and sites may not be treated with this product in California until approval is received:

- Use of 1.0 ml of this product per 2 to 3 inches of trunk diameter for injection and frill applications.
- Use of this product for cut stump treatments on the following species:

Coyotebrush

Poplar

Dogwood

Russian Olive

Hickory

Sweetgum

Maple

Sycamore

Product is protected by U.S. Patent No. 3,799,758 and U.S. Patent No. 4,405,531.

Other patents are pending.

No license granted under any non-U.S. patent.

EPA Reg. No. 524-343

In case of an emergency involving this product. Call Collect. day or night. (314) 694-4000.

© MONSANTO COMPANY 1990

1990-1

892.38-000.88/CG

MONSANTO COMPANY AGRICULTURAL PRODUCTS ST. LOUIS, MISSOURI, 63167 U.S.A.





The 2,4-D Amine Weed Killer

ACTIVE INGREDIENT:

\*2,4-Dichlorophenoxyacetic acid equivalent 38.9% by weight or 3.8 pounds per gallon

\*Isomer specific by AOAC method No. 6.D01-5

E.P.A. Reg. No. 264-2AA

Est. No. 264-MO-01

### KEEP OUT OF REACH OF CHILDREN DANGER **PELIGRO**

PRECAUTION AL USARIO: Si usted no lee ingles, no use este producto hasta que la etiqueta le haya sido explicado ampliamente. For PRODUCT USE Information Call 1-800-334-9745

For EMERGENCY Information ONLY Call 24 Hours A Day 1-800-334-7577.

# STATEMENT OF PRACTICAL TREATMENT

IF ON SKIN: Wash skin with plenty of soap and water. Remove contaminated clothing. Get medical attention.

IF SWALLOWED: If patient is conscious and alert, give 2 to 3 glasses of water or milk to drink. If available, give one tablespoon of Syrup of Ipecac to induce vomiting. Alternatively, induce vomiting by touching back of throat with finger. Do not make an unconscious

IF IN EYES: Flush with water for at least 15 minutes. Get medical attention, PREFERABLY AN OPTHAMOLOGIST.

IF INHALED: Move to an unconfaminated area. Get medical attention.

NOTE TO PHYSICIAN

This product contains a phenoxy herbicidal chemical. There is no specific antidate. All reatments should be based on observed signs and symptoms of distress in the patient. Overexposure to materials other than this product may have occurred.

### PRECAUTIONARY STATEMENTS

### DANGER

# HAZARDS TO HUMANS AND DOMESTIC ANIMALS

Harmful if swallowed. May be fatal if absorbed through the skin Canees irreversible eye damage. Avoid breathing vapors or spray mist. Do not get in eyes, on skin, or on clothing. When handling this product, wear goggles or safety glasses, protective clothing and chemical resistant gloves. Wash thoroughly with soap and wash after handling and before eating, drinking or using tobacco. Remove

## ENVIRONMENTAL HAZARDS

This product is toxic to aquatic invertebrates. Drift or wholf may adversely affect aquatic invertebrates and non-target plants. Do not apply directly to water except as specified on this laber. Do not contaminate water when disposing of equipment washwaters. Do not apply when weather conditions favor drift from treated areas. Do not use the same spray equipment for other purposes unless

Do not contaminate water used for irrigation or domestic purposes (except as specifically recommended on this label) especially in areas where grapes, cotton, tomatoes or other susceptible plants are grown.

Do not treat irrigation ditches in areas where water will be used to overhead (sprinkler) irrigate susceptible crops especially grapes,

MIXING AND LOADING: Most cases of ground water contamination involving phenoxy herbicides such as 2,4-D have been associated with mixing/loading and disposal sites. Caution should be exercised when handling 2,4-D pesticides at such sites to prevent contamination of ground water supplies. Use of closed systems for mixing or transferring this pesticide will reduce the probability of spills. Placement of the mixing/loading equipment on an impervious pad to contain spills will help prevent ground water contamination.

Do not apply WEEDAR® 64 Broadleaf Herbicide directly to, or permit to drift onto cotton, okra, grapes tomatoes, fruit trees, vegetables, flowers or other desirable crop or ornamental plants which are susceptible to 2,4-D herbicide. Do not apply near susceptible plants since very small quantities of the 2,4-D will cause severe injury during the growing or dormant periods. Crops contacted by WEEDAR® 64 Broadleaf Herbicide sprays or spray drift may be killed or suffer significant stand loss with extensive

Do not apply when a temperature air inversion exists. Such a condition is characterized by little or no air movement and an increase in air temperature with an increase in height. In humid regions, a fog or mist may form. An inversion may be detected by producing a smoke column and checking for a layering effect. If questions exist pertaining to the existence of an inversion, consult with local

Use coarse sprays to minimize drift. Do not apply with hollow cone-type insecticide or other nozzles that produce fine spray droplets. Drift from aerial or ground application may be reduced by: (1) applying as near to the target as possible in order to obtain coverage; (2) by increasing the volume of spray mix per acre; (3) by decreasing the pounds of pressure at the nozzle tips; and (4) by using nozzles which produce a coarse spray pattern; (5) by not applying when wind is blowing toward susceptible crops or valuable plants.

### DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling. Read entire label before using this label.

# GENERAL WORKER PROTECTION STATEMENTS

Do not apply this product in such a manner as to directly or through drift expose workers or other persons. The area treated must be vacated by unprotected persons. Do not enter treated areas without protective clothing until sprays have dried. Because certain states may require more restrictive reentry intervals for various crops treated with this product, consult your State Department of Agriculture for further information. Written or oral warnings must be given to workers who are expected to be in a treated area or in an area about to be treated with this product. Advise workers to stay out of fields during application and until sprays have dried. Regular long-sleeved work clothing should be worn when working in treated fields. See PRECAUTIONARY STATEMENTS, STATEMENT OF PRACTICAL TREATMENT and NOTE TO PHYSICIAN for information on accidental exposures. When oral warnings are given, warnings shall be given in a language customarily understood by workers. Oral warnings must be given if there is reason to believe that written warnings cannot be understood by workers. Written warnings must include the following information: appropriate signal word (DANGER - PELIGRO), area treated with WEEDAR® 64 Broadleaf Herbicide, date of application, appropriate protective clothing, and reentry

## STORAGE AND DISPOSAL

### STORAGE

-01

a af

sinns

mist.

nd

VΘ

101

not not unless

ii in

rangs,

Juialed

revent

ס ניייני

y near

i sive

ease in

ocal

1 1. nees,

!S

Do not contaminate water, food or feed by storage or disposal. Store in original container in a dry secured storage area. Keep container

### PESTICIDE DISPOSAL

Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal law and may contaminate ground water. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

Triple rinse or (equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

## GENERAL CAUTIONS AND RESTRICTIONS

Do not apply WEEDAR® 64 Broadleaf Herbicide through any type of irrigation system.

Do not use in or near a greenhouse.

# RESTRICTIONS AND LIMITATIONS FOR USE ON CEREAL GRAINS

For aerial application on grain, apply WEEDAR® 64 Broadleaf Herbicide in 3 to 10 gallons of water per acre.

For ground application a minimum of 10 to 15 gallons of water per acre is recommended for proper spray coverage.

Do not permit dairy animals or meat animals being finished for slaughter to forage treated grain fields within 2 weeks after treatment.

Do not feed treated straw to livestock if an emergency treatment as described below is applied.

# RESTRICTIONS AND LIMITATIONS FOR USE ON CORN AND SORGHUM

Do not forage or feed fodder for 7 days following application.

# RESTRICTIONS AND LIMITATIONS FOR USE IN FALLOWLAND AND CROP STUBBLE

Do not plant any crop for 3 months after treatment or until chemical has disappeared from the soil.

# RESTRICTIONS AND LIMITATIONS FOR USE IN PASTURES AND RANGELANDS

Do not graze (dairy) cattle in treated areas for 7 days after application.

Do not cut forage for hay within 30 days of application.

Do not permit dairy animals or meat animals being finished for slaughter to forage treated fields within 3 days of slaughter.

# RESTRICTIONS AND LIMITATIONS FOR USE ON CONSERVATION RESERVE PROGRAM AREAS:

Use at least 2 gallons of water per acre by air and 5 gallons of water per acre by ground.

Do not harvest or graze treated Conservation Reserve Program areas.

Do not apply to grasses in the boot to dough stage if grass seed production is desired.

# RESTRICTIONS AND LIMITATIONS FOR USE ON GRASSES FOR SEED PRODUCTION

 $D_0$  not graze dairy animals or cut forage for hay within 7 days of application.

•bir

blu

SI

**(**u

Er

Pέ

# RESTRICTIONS AND LIMITATIONS FOR USE ON NON-CROPLAND

Do not graze dairy animals for 7 days following application.

Use sufficient gallonage for thorough and uniform coverage.

# RESTRICTIONS AND LIMITATIONS FOR USE IN STONE FRUIT AND NUT ORCHARDS

Do not apply immediately before irrigation and withhold irrigation for 2 days before and for 3 days after treatment.

Do not allow spray to drift onto or contact foliage, fruit, stems, trunks of trees or exposed roots as injury may result.

Do not apply to newly established or young orchards. Trees must be at least 1 year old and in vigorous condition.

Do not graze or feed cover crops from treated orchards.

Do not make more than 2 applications per year.

Do not harvest stone fruit within 40 days of application.

Do not harvest nuts within 60 days of application.

### MIXING INSTRUCTIONS

Mix WEEDAR® 64 Broadleaf Herbicide only with water, unless otherwise directed on this label. Add about one-half the water to the mking tank, then add WEEDAR® 64 with agitation and finally the rest of water with continuing agitation.

NOTE: Adding oil, wetting agent, or other surfactants to the spray may increase effectiveness on weeds but also may reduce

\* WEEDAR\* 64 Broadleaf Herbicide is to be tank mixed with fertilizers or with other pesticides, compatibility should be tested prior to mixing. To test for compatibility, use a small container and mix a small amount (0.5 to 1 qt) of spray, combining all ingredients in the same ratio as the anticipated use. If any indications of physical incompatibility develop, do not use this mixture for spraying.

Read and follow all directions and precautions on this label and on the labels of any products for which a tank mixture is being APPLICATION PROCEDURES

Apply by air or ground equipment in sufficient gallonage to obtain adequate coverage, except as otherwise directed on this label. Lee 2 or more gallons of water per acre for aerial application and 10 or more gallons of water per acre for ground application.

WURY TO CROPS FROM THIS HERBICIDE MAY OCCUR. IF YOU ARE NOT PREPARED TO ACCEPT SOME DEGREE OF CROP

pop varieties vary in response to 2,4-D and some are easily injured. Apply WEEDAR® 64 Broadleaf Herbicide only to varieties known to tolerant to 2,4-D. If you are uncertain concerning tolerant varieties or local use situations that may affect crop tolerance to 2,4-D, ansult your seed company, state Agricultural Extension Service or qualified crop consultant for advice.

sure that use of this product conforms to all applicable laws, rules and regulations. Certain states have restrictions pertaining to pplication distances from susceptible crops. The applicator should become familiar with these laws, rules or regulations and follow

ggarticks
Ithistle feeweed imon cocklebur imon burdock mon evening primrose mon lambsquarters y galinsoga priweed weed



Perennial Weeds
-----------------

*bindweed (hedge, field, European)	*goldenrod	**nettles (including stinging)
blue lettuce *Canada thistle	*ground ivy	*orange hawkweed
catnip	healall *hoary cress	plantains sowthistle (perennial)
chicory	•ironweed	*vervains
dandelion *docks	Jerusalem-artichoke many flowered aster	*wild garlic
*dogbanes	many noncred aster	*wild onion

<sup>\*</sup>These species may require repeated applications and/or use of the higher rate recommended on this product label even under ideal conditions for application.

### SPECIFIC USE DIRECTIONS

.ce

to the

ing

**30P** 

3 )

( ) ); √

### CEREAL GRAINS

CROP	AMOUNT OF WEEDAR® 64 PER ACRE	DIRECTIONS
Wheat, Barley, Oats and Rye (not underseeded with legumes) Postemergence Annual and biennial broadleaf weeds Perennial broadleaf weeds	1/2 to 2 pints* 1 to 2 pints*	Apply after grain is fully tillered (usually 4 to 8 incheshigh) but not forming joints in the stem. Do no spray grain in the boot to dough stage.
Wheat, Barley, Oats and Rye (underseeded with legumes)	1/4 to 1/2 pint*	Apply after grain is 8 inches tall. Do not spray grain in boot to dough stage. Do not spray affalfa or sweet clover unless the infestation is severe and injury to these legumes can be tolerated.
Emergency weed control in Wheat Perennial broadleaf weeds	3 pints	Apply when weeds are approaching bud stage, afte the grain dough stage. Do not spray during the boot to dough stage. The 3 pints per acre application can product injury to wheat. Balance the severity of your weed problem against the possibility of crop damage. Where perennial weeds are scattered, spot treatment is suggested to minimize the extent of crop injury.

<sup>\*</sup>Use the lower rate if small annual and biennial weeds are the major problem. Use the higher rate if perennial weeds or annual and biennial weeds are present which are in the hard-to-kill categories as determined by local experience. The higher rates increase the risk of grain injury and should be used only where the weed control problem justifies the grain damage risk. Do not apply WEEDAR® 64 to grain in the seedling stage.

<sup>\*\*</sup>Control of pigweeds in the High Plains area of Texas and Oklahoma may not be satisfactory with this product.

<sup>\*\*\*</sup>Not registered for control of musk thistle in California.

# CORN AND SORGHUM

CROP	AMOUNT OF WEEDAR® 64	
CORN (Field and Sweet)	PER ACRE	
Preplant	1 to 2 pints	To control emerged broadleaf weed seedlings existing cover crops prior to planting corn, apply 7 to 4 days before planting. Do not use on links of the control of the contr
Preemergence	240.4	soil, or where soil moisture is inadequate for normal weed growth. Use high rate for less susceptible weeds or cover crops such as a susceptible was a susceptible with the susceptible was a su
Postemergence	. 1	Apply 3 to 5 days after planting but before corn soil moisture is low
Annual broadleaf weeds Perennial broadleaf weeds	1/2 to 1 pint 1 to 1 1/2 pints	Apply when weeds are small and corn is less than a inches tall (to top of canopy). When corn is over 8 to light and the corn is less than 8 to light and 1
irain Sorghum (Milo)	Į į	oud to bloom stage. Do not spray corn in the assel to dough stage. Corn treated with 2,4-D nay become temporarily brittle. Winds or cultivation hay cause stalk breakage during the period of time the corn is brittle.
ostemergence	is no	pply when sorghum is 6 to 15 inches tall. If sorghum taller than 8 inches to top of the canopy, use drop ozzles and keep spray off the foliage. Do not eat during the boot, flowering or dough

# RICE, SUGARCANE, FALLOWLAND AND CROP STUBBLE

Rice	AMOUNT OF WEEDAR	
Sugarcane	1 to 2 1/2 pints	Apply when rice is in the late tillering stage of development at the time of first joint development. Device in the late tillering stage of the stag
Preemergence Postemergence	4 pints	Apply before
Fallowland and Crop Stubble Annual broadleaf weeds	1 1/2 to 2 pints	May by DO NOT USE IN CALIFORNIA
Biennial broadleaf weeds	1 to 2 pints	Use the lower rate when weeds are small (2 to 3 inches tall) and actively growing. Use the higher rate on older and drought-stressed plants.
erennial broadleaf weeds	2 to 4 pints	spray while musk thistles or other biennial species are in the seedling to rosette stage and before flower in the spring during rosette stage. Use the highest rate in the fall or after flower.
ild garlic and onion in crop stubble	2 to 6 pints	vegetative and the bud to bloom stage as we'll
or of Studdle	4 to 6 pints	least 2 weeks after treatment, or until tops are dead.  Apply to new regrowth of wild garlic or onion which occurs in the fall following harvest of small grains,

Mix 2 to 3 fluid ounces of WEEDAR® 64 Broadleaf Herbicide in 3 gallons of water. Wet all weeds and stems thoroughly. For best results,

### FORESTRY - TREE INJECTION For controlling species such as alder, aspen, birch, blackgum, cherry, oak, sweetgum, and tulip poplar

٧

٧

A

a ٧

IT

H u S

С s F

2 Y ١

Make injections as near to the root collar as possible, using one injection per inch of trunk dbh (4 1/2 feet). For resistant species such Make injections as near to the root contains as possible, using one injection per mon or trunk upin (4-1/2 reet). For resistant species such as hickory, injections should overlap. For best results, injections should be made during the growing season, May 15th through

For Dilute Injection: Mix 1 gallon of WEEDAR® 64 Broadleaf Herbicide in 19 gallons of water for dilute injections.

For Concentrate Injections: Use 1 to 2 ml of concentrate WEEDAR® 64 Broadleaf Herbicide per injection. The injection bit must

WEEDS IN CROP	STONE FRUIT AND NUT	ONCHARDS
Annual broadleaf weeds	PER ACRE	DIRECTIONS
	·	For control of weeds on the orchard floor, apply using coarse sprays and low pressure in sufficient volume of water to obtain thorough wetting of weeds. Treat when weeds are small and actively growing. Do not use on light, sandy soil. DO NOT USE IN CALIFORNIA.

### WEEDS AND BRUSH IRRIGATION CANAL DITCHBANKS (Seventeen Western States: Arizona, California, Colorado, Idaho, Kansas, Montana, Nebraska, New Mexico, Nevada, North Dakota, Oklahoma, Oregon, South Dakota, Texas, Utah, Washington, and Wyoming).

For control of annual and perennial broadleaf weeds, apply 1 to 2 quarts of WEEDAR® 64 Broadleaf Herbicide per acre in approximately 20 to 100 gallons per acre. Treat when weeds are young and actively growing before the bud or early bloom stage. For harder-to-control weeds, a repeat spray after 3 to 4 weeks using the same rates may be needed for maximum results. Apply no more than two treatments

For woody brush and patches of perennial broadleaf weeds, mix 1 gallon of WEEDAR® 64 in 150 gallons of water. Wet foliage SPRAYING INSTRUCTIONS

Apply with low pressure (10 to 40 psi) power spray equipment mounted on a truck, tractor, or boat. Apply while traveling upstream to avoid accidental concentration of chemical into water. Spray when the air is fairly claim, 5 mph or less. Do not use on small canals (less

Boom spraying onto water surface must be held to a minimum and no cross-stream spraying to opposite banks should be permitted. When spraying shoreline weeds, allow no more than 2 foot overspray onto water with an average of less than 1 foot overspray to prevent introduction of greater than negligible amounts of chemical into the water.

Do not allow dairy animals to graze on treated areas for at least 7 days after spraying. Water within treated banks should not be fished.

## AQUATIC WEED CONTROL

For use in ponds, lakes, reservoirs, marshes, bayous, drainage ditches, canals, rivers and streams that are NOTICE TO APPLICATORS

State and Local Coordination: Before application, coordination and approval of local and state authorities may be required,

Fish Toxicity - Oxygen Ratio: Fish breathe oxygen in the water and a water - oxygen ratio must be maintained. Decaying weeds use up oxygen. To the lake or pond at one time. For large use up oxygen. To avoid fish kill from decaying plant material do not treat more than one half the lake or pond at one time. For large bodies of weed infantable with the lake or pond at one time. For large bodies of weed infested waters leave buffer strips of at least 100 feet wide and delay treatment of these strips for 4 to 5 weeks or until

Wind Velocity - Ground or Surface Application: Do not apply when wind speeds are at or above 10 mph. Air Application: Do not apply when wind speeds are at or above 10 mph. Air Application: Do not apply when wind speeds are at or above 5 mph. The restrictions do not apply to subsurface applications used in weed control programs.

Irrigation: Delay the use of treated waters for irrigation for three weeks after treatment unless an approved assay shows that the water does not contain a seas where water will be used to overhead water does not contain more than 0.1 ppm 2,4-D acid. Do not treat irrigation ditches in areas where water will be used to overhead 108

# ESTABLISHED GRASS PASTURES, RANGELAND, AND CONSERVATION RESERVE PROGRAM AREAS

		LAG
WEEDS	AMOUNT OF WEEDAR® 64 PER ACRE	DIRECTIONS
Annual broadleaf weeds	2 pints	Apply when woods are a "
Biennial and perennial broadleaf weeds	2 to 4 pints	prior to bud stage. Spray while musk thistles or other biennial species are in the seedling to rosette stage and before flower stalks become apparent. The lower rate can be used in the spring during rosette stage. Use the highest rate in the fall or after flower stalks have developed. Do not apply to newly seeded areas until grass is well established. Do not apply to grass in the early boot through milk stage if grass seed production is desired. Bentgrass and legumes may be injured by this treatment.

# CONSERVATION RESERVE PROGRAM AREAS

		HOGHAM AREAS
WEEDS	AMOUNT OF WEEDAR® 64 PER ACRE	
Annual broadleaf weeds		DIRECTIONS
In young grasses	1/2 to 1 pint	Apply to actively growing annual broadleaf weeds. Use 1/2 to 1 pint when weeds are small; use higher
In established grasses	1/2 to 2 pints	with fewer than 6 leaves or prior to tillering, as excessive injury may result. Do not apply more than 1 pint until grasses are well established.
Biennial and perennial broadleaf weeds	2 to 4 pints	1-7 may rosum.
In established grasses		Treat when biennial weeds are in the seedling to rosette stage and before flower stalks become apparent. Treat perennial weeds in the bud to bloom stage. Apply to actively growing weeds.

# GRASSES FOR SEED PRODUCTION

		HODOCHON
WEEDS	AMOUNT OF WEEDAR® 64 PER ACRE	DIRECTIONS
Annual and perennial broadleaf weeds	2 to 4 pints	Apply to established stands in spring from tiller to early boot stage. Do not spray in boot stage. New spring seedings may be treated with the lower rate after grass seedlings have at least 5 leaves. Perennial weed regrowth may be treated in the fall. DO NOT USE IN CALIFORNIA.

0 0

3

عد عد عا عا

# fencerows, roadsides, drainage ditches, golf courses, cemeteries, parks, turfgrass, and other grass areas

5 we, and other grass areas		
WEEDS	AMOUNT OF WEEDAR® 64 PER ACRE	DIRECTIONS
Annual broadleaf weeds	2 to 4 pints	Treat when weeds are yours and it
Biennial and perennial broadleaf	4 to 8 pints	not flowering at application. Do not use on susceptible southern grasses such as St. Augustia
		apply to newly seeded areas until grass is well established. Bentgrass, clover, legumes and dichondria may be injured by this treatment.

# SPOT TREATMENT IN NON-CROP AREAS

Mix 2 to 3 fluid ounces of WEEDAR® 64 Broadleaf Herbicide in 3 gallons of water. Wet all weeds and stems thoroughly. For best results,

### FORESTRY - TREE INJECTION For controlling species such as alder, aspen, birch, blackgum, cherry, oak, sweetgum, and tulip poplar

Make injections as near to the root collar as possible, using one injection per inch of trunk dbh (4 1/2 feet). For resistant species such Make injections as near to the root conar as possible, using one injection per mon or trunk upin (4-1/2 reet). For resistant species such as hickory, injections should overlap. For best results, injections should be made during the growing season, May 15th through

For Dilute Injection: Mix 1 gallon of WEEDAR® 64 Broadleaf Herbicide in 19 gallons of water for dilute injections.

For Concentrate Injections: Use 1 to 2 ml of concentrate WEEDAR® 64 Broadleaf Herbicide per injection. The injection bit must

STONE FRUIT AND NUT ORCHARDS		
WEEDS IN CROP	AMOUNT OF WEEDAR® 64	
Annual broadleaf weeds	0	DIRECTIONS
		For control of weeds on the orchard floor, apply using coarse sprays and low pressure in sufficient volume of water to obtain thorough wetting of weeds. Treat when weeds are small and actively growing. Do not use on light, sandy soil. DO NOT USE IN CALIFORNIA.
WEEDS AND		OALII ORINIA.

### WEEDS AND BRUSH IRRIGATION CANAL DITCHBANKS (Seventeen Western States: Arizona, California, Colorado, Idaho, Kansas, Montana, Nebraska, New Mexico, Nevada, North Dakota, Oklahoma, Oregon, South Dakota, Texas, Utah, Washington, and Wyoming).

For control of annual and perennial broadleaf weeds, apply 1 to 2 quarts of WEEDAR® 64 Broadleaf Herbicide per acre in approximately 20 to 100 gallons per acre. Treat when weeds are young and actively growing before the bud or early bloom stage. For harder-to-control weeds, a repeat spray after 3 to 4 weeks using the same rates may be needed for maximum results. Apply no more than two treatments

For woody brush and patches of perennial broadleaf weeds, mix 1 gallon of WEEDAR® 64 in 150 gallons of water. Wet foliage SPRAYING INSTRUCTIONS

Apply with low pressure (10 to 40 psi) power spray equipment mounted on a truck, tractor, or boat. Apply while traveling upstream to avoid accidental concentration of chemical into water. Spray when the air is fairly claim, 5 mph or less. Do not use on small canals (less

Boom spraying onto water surface must be held to a minimum and no cross-stream spraying to opposite banks should be permitted. When spraying shoreline weeds, allow no more than 2 foot overspray onto water with an average of less than 1 foot overspray to

Do not allow dairy animals to graze on treated areas for at least 7 days after spraying. Water within treated banks should not be fished.

# AQUATIC WEED CONTROL

For use in ponds, lakes, reservoirs, marshes, bayous, drainage ditches, canals, rivers and streams that are NOTICE TO APPLICATORS

State and Local Coordination: Before application, coordination and approval of local and state authorities may be required,

Fish Toxicity - Oxygen Ratio: Fish breathe oxygen in the water and a water - oxygen ratio must be maintained. Decaying weeds use up oxygen Toxicity - Oxygen Ratio: Fish breathe oxygen in the water and a water - oxygen ratio must be maintained. Decaying weeds use up oxygen. To avoid fish kill from decaying plant material do not treat more than one half the lake or pond at one time. For large bodies of weed inferted uses a large bodies of weed inferted uses a large bodies of weed inferted uses a large bodies of the large bodies of weed inferted uses a large bodies of the large bod bodies of weed infested waters leave buffer strips of at least 100 feet wide and delay treatment of these strips for 4 to 5 weeks or until the dead vegetation has decomposed.

Wind Velocity - Ground or Surface Application: Do not apply when wind speeds are at or above 10 mph. Air Application: Do not apply when wind speeds are at or above 10 mph. Air Application: Do not apply when wind speeds are at or above 5 mph. The restrictions do not apply to subsurface applications used in weed control programs.

Irrigation: Delay the use of treated waters for irrigation for three weeks after treatment unless an approved assay shows that the water does not contain a seas where water will be used to overhead water does not contain more than 0.1 ppm 2,4-D acid. Do not treat irrigation ditches in areas where water will be used to overhead sprinkler irrigate susceptible crops especially grapes, tomatoes and cotton. 108

Potable Water: Delay the use of treated water for domestic purposes for a period of three weeks or until such time as an approved assay shows that the water contains no more than 0.1 ppm 2,4-D acid.

# Water Hyacinth (Eichornia crassipe) - Directions For Use

WEEDAR® 64 will control water hyacinth with surface and air applications.

S.

zħ

JS!

÷

:ely

irol

n ø

(less

ay 10

Amounts to Use: 2 to 4 quarts (4 lb. acid equivalent per gallon) per acre. Spray the weed mass only. Use 4 quarts when plants

When To Apply: Spray when water hyacinth plants are actively growing. Repeat as necessary to kill regrowth and hyacinth plants

How To Use - Surface Application: Use power sprayers operated with a boom or spray gun mounted on a boat, tractor or truck. Thorough wetting of foliage is essential for maximum control. Use 100 to 400 gal./A of spray mixture. Special precautions such as the use of low pressure, large nozzles and thickening agents should be taken to avoid spray drift in areas of sensitive crops. For DIRECTASPRAM operation use WEEDAR® 64 with 1 pint of drift control agent in 50 to 100 gallons of water. For other applications, follow the drift control agent label for mixing directions. Air Application: Use drift control spray equipment or thickening agents mixed into the spray solution. Apply 1.0 gallon per acre of WEEDAR® 64 through standard boom systems with a minimum of 5 gallons of spray mix per acre. For MICROFOIL® drift control spray systems, apply WEEDAR® 64 in 12 to 15 gallons spray mix per acre.

			04 III 12 to 15 gain	ons spray mix	per acre.	. James per acre.
2,4-D Acid Equivalent WEEDAR® 64	1/2 lb. 1 pt.	1 lb. 2 pts.	2 lbs.	3 lbs.	4 lbs.	
	· pi.	Z pis.	2 qts.	3 qts.	4 ats.	
Water Milfeil /Marriage						

# Water Milfoil (Myriophyllum spicatum) - Directions For Use

For Eurasian Water Milfoil in programs conducted by the Tennessee Valley Authority in dams and reservoirs of the TVA system.

WEEDAR® 64 will control water milfoil with surface, subsurface and air applications.

How To Use: To control water milfoil when less than 5 gallons of concentrate per acre is recommended, dilute the concentrate with water to apply a minimum of 5 gallons of spray mix per acre. Do not treat within 1/2 mile of potable water intakes. Shoreline areas should be treated by sub-surface injection applied by boat to avoid aerial drift. Do not apply when weather conditions favor drift from target area. Do not contaminate water by cleaning of equipment washwaters.

Open Water Areas: To reduce contamination and prevent undo exposure to fish and other aquatic organism, do not treat water

Amounts To Use: Apply 2.5 to 10 gallons of WEEDAR® 64 per acre. The higher rate is used in areas of greater water exchange.

When To Apply: For best results, apply in spring or early summer when milfoil starts to grow. This timing can be checked by sampling

Subsurface Application: Apply 2.5 to 10 gallons of WEEDAR® 64 per acre as a concentrate directly into the water through boat

Surface Application: Apply 2.5 to 10 gallons of WEEDAR® 64 per acre in a minimum spray volume of 5 gallons mix per acre.

Air Application: Use drift control spray equipment or thickening agents mixed into the spray solution. Apply 2.5 to 10 gallons per acre of WEEDAR® 64 through standard boom systems with a minimum of 5 gallons of spray mix per acre. For MICROFOIL® drift control spray systems apply WEEDAR® 64 in 12 to 15 gallons spray mix per acre.

# LIMITED WARRANTY AND DISCLAIMER

The manufacturer warrants that this product conforms to the chemical description on the label; that this product is reasonably fit for the purposes set forth in the directions for use when it is used in accordance with such directions; and that the directions, warnings and other statements on this label are based upon responsible experts' evaluation of reasonable tests of effectiveness, of toxicity to other statements on this laber are based upon responsible experience. Tests have not been made on all laboratory animals and to plants, and of residues on food crops, and upon reports of field experience. Tests have not been made on all laboratory animals and to plants, and of residues on food crops, and upon reports of field experience. Tests have not been made on all laboratory animals and to plants, and or residues on 1000 crops, and upon reports or field expensation. Tests flat and took of all varieties or in all states or under all conditions. THE MANUFACTURER NEITHER MAKES NOR INTENDS, NOR DOES IT AUTHORIZE VARIED WARD AND IT EXPRESS! Y EXCLUDE. ANY AGENT OR REPRESENTATIVE TO MAKE, ANY OTHER WARRANTIES, EXPRESS OR IMPLIED, AND IT EXPRESSLY EXCLUDES AND DISCLAIMS ALL IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

THIS WARRANTY DOES NOT EXTEND TO, AND THE BUYER SHALL BE SOLELY RESPONSIBLE FOR, ANY AND ALL LOSS OR DAMAGE WHICH RESULTS FROM THE USE OF THIS PRODUCT IN ANY MANNER WHICH IS INCONSISTENT WITH THE LABEL

BUYER'S EXCLUSIVE REMEDY AND MANUFACTURER'S OR SELLER'S EXCLUSIVE LIABILITY FOR ANY AND ALL CLAIMS. LOSSES, DAMAGES, OR INJURIES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT, WHETHER OR NOT BASED IN CONTRACT, NEGLIGENCE, STRICT LIABILITY IN TORT OR OTHERWISE SHALL BE LIMITED, AT THE MANUFACTURER'S OPTION, TO REPLACEMENT OF, OR THE REPAYMENT OF THE PURCHASE PRICE FOR, THE QUANTITY OF PRODUCT WITH RESPECT TO WHICH DAMAGES ARE CLAIMED. IN NO EVENT SHALL MANUFACTURER OR SELLER BE LIABLE FOR SPECIAL, INDIRECTOR CONSEQUENTIAL DAMAGES RESULTING FROM THE USE OR HANDLING OF THIS PRODUCT.

### NOTICE TO BUYER

Purchase of this material does not confer any rights under patents governing this product or the use thereof in countries outside of the

THIS SPECIMEN LABEL IS INTENDED FOR USE ONLY AS A GUIDE IN PROVIDING GENERAL INFORMATION REGARDING THE DIRECTIONS, WARNINGS AND CAUTIONS ASSOCIATED WITH THE USE OF THIS PACKAGE REFORE USING AGRICULTURAL CHEMICAL, ALWAYS FOLLOW THE LABEL INSTRUCTIONS ON THE PACKAGE BEFORE USING.

Rhône-Poulenc Ag Company P.O. Box 12014, 2 T.W. Alexander Drive Research Triangle Park, North Carolina 27709

Form No. 93482 Printed USA - 9/91

WEEDAR and MICROFOIL are registered trademarks of RHONE-POULENC. DIIRECTA-SPRA is a trademark of RHONE-POULENC. ©1991 Rhône-Poulenc Ag Company Made in USA.

EPA Approval: 6/24/91

### **APPENDIX 2**

Generic Data Requirements and Unacceptable
Studies for 2,4-D Reregistration

GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS TABLE A

Data Requirement	Test Substance	Use Patterns	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.490 Wildlife and Aquatic Organisms						
AVIAN AND MAMMALIAN TESTING						
71-1 - Acute Avian Oral Toxicity	TGAI	A,B,C,D,G	Partially	00160000	Yes (2)	9 Months
71-2 - Avian Subacute Dietary Toxicity - Upland Game Bird, and	TGAI	A,B,C,D,G	No		Yes	9 Months
- Waterfowl	TGAI	A,B,C,D,G	No		Yes	9 Months
71-3 - Wild Mammal Toxicity	TGAI	A,B,G	o		No (3)	
71-4 - Avian Reproduction	TGAI	A,B,G	o N		Reserved (4)	
71-5 - Simulated and Actual Field Testing						
- Mammals, and	TEP	A,B,G	No		Reserved (5)	
- Birds	TEP	A,B,G	No		Reserved (5)	

GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS **TABLE A** 

Data Requirement	Test Substance	Use	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.490 Wildlife and Aquatic Organisms - Continued					·	
72-6 - Aquatic Organism Accumulation	TGAI	A,B,C,D	No		Yes (15)	12 Months
72-7 - Simulated and Actual Field Testing - Aquatic Organisms	TEP	A,B,C,D	No		Reserved (4)	

- (1) Data must be submitted within the indicated timeframes, which begin on receipt of the Guidance Document.
- (2) The Agency has acceptable data on 2,4-D acid. Data must be submitted on salts, amines and esters.
- (3) Not currently a requirement.
- (4) Reserved pending receipt and review of all environmental fate data.
- (5) Reserved pending receipt and review of all environmental fate data. This study is not required for 2,4-D acid, 2,4-D Lithium Salt, 2,4-D Sodium Salt, and 2,4-D Alkanolamine Salt because of this use.
- (6) The Agency has acceptable data on 2,4-D Propylene Glycol Butyl Ether Ester, and 2,4-D acid. Data must be submitted on all other salts, amines and esters.
- (7) The Agency has acceptable data on 2,4-D Propylene Glycol Butyl Ether Ester and 2,4-D acid. Data must be submitted on all other salts, amines and esters. Testing is required for 2,4-D Butoxypropyl Ester products having 67.2 percent acid equivalent.

GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS **TABLE A** 

Data Requirement	Test Substance	Use Patterns	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.490 Wildlife and Aquatic Organisms - Continued	·		·			
AQUATIC ORGANISM TESTING						
72-1 - Freshwater Fish Toxicity Warmwater	TGAI	A,B,C,D,G	Partially	40098001	Yes (6)	9 Months
Warmwater	TEP	A,B,C,D	Partially	00050678, 00050681 00050715, 00054025 00054045, 40098001, 40600203	Yes (8)	9 Months
Coldwater	TGAI	A,B,C,D,G	Partially	40098001	Yes (6,7)	9 Months
Coldwater	TEP	A,B,C,D	Partially	00050669, 00050712 00050713, 00053986 00050674, 00053996	Yes (9)	9 Months
72-2 - Acute Toxicity to Freshwater Invertebrates	TGAI TEP	A,B,C,D,G A,B,C,D	Partially Partially	00102908, 40098001 00054025, 40098001	Yes (10) Yes (11)	9 Months 9 Months
72-3 - Acute Toxicity to Estuarine and Marine Organisms	TGAI	A,B,C,D,G	Partially	40228401	Yes (12)	12 Months
72-4 - Fish Early Life Stage, and Aquatic Invertebrate Life-Cycle	TGAI	A,B,C,D	o N		Yes (13)	12 Months
72-5 - Fish - Life Cycle	TGAI	A,B,C,D	No		Reserved (14)	

TABLE A
GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS

Data Requirement	Test	Use	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.340 Toxicology						
ACUTE TESTING						~.
81-1 - Acute Oral Toxicity - Rat	ACID-TGAI		Yes	00101605, 00101591.	o Z	
	AMINE-TGAI ESTER-TGAI		No Partially	00101595, 00101601 00138284, 40629801	Yes (2) Yes (3)	9 Months 9 Months
81-2 - Acute Dermal Toxicity - Rabbit	ACID-TGAI AMINE-TGAI		Yes	00101596	No Vec (2)	o Managhan
	ESTER-TGAI		Partially	00101592, 00101600 00138284, 40629802	Yes (3)	9 Months
81-3 - Acute Inhalation Toxicity - Rat	ACID-TGAI AMINE-TGAI		Yes	00161660	No Yes (2)	9 Months
81-4 - Eye Irritation - Rabbit	ACID-TGAI AMINE-TGAI ESTER-TGAI		Partially No No Partially	40352702, 40629804	Yes (4)  Yes  Yes (2)  Yes (4)	9 Months 9 Months 9 Months

GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS TABLE A

Data Requirement	Test Substance	Use	Does EPA Have Data to Satisfy This Requirement?	Bibliographic	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.340 Toxicology - Continued						
81-5 - Dermal Irritation - Rabbit	ACID-TGAI AMINE-TGAI ESTER-TGAI		No No Partially	40352703, 40629805	Yes Yes (2) Yes (4)	9 Months 9 Months 9 Months
81-6 - Dermal Sensitization - Guinea Pig	ACID-TGAI AMINE-TGAI ESTER-TGAI		Yes No Partially	00161659 00156564, 00156637 40352704, 40629806	No Yes (2) Yes (4)	9 Months 9 Months
81-7 - Acute Delayed Neurotoxicity - Hen	ACID-TGAI AMINE-TGAI ESTER-TGAI		8		No (5) No (5) No (5)	
SUBCHRONIC TESTING						
82-1 - 90-Day Feeding: - Rodent, and	ACID-TGAI AMINE-TGAI ESTER-TGAI		0 <b>0</b> 0		No (6) Yes Yes	15 Months 15 Months
- Non-Rodent (Dog)	ACID-TGAI AMINE-TGAI ESTER-TGAI		0 0 0 2 X Z		No (7) Yes Yes	18 Months 18 Months

TABLE A
GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS

Data Requirement	Test Substance	Use	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.340 Toxicology - Continued						
82-2 - 21-Day Dermal	ACID-TGAI AMINE-TGAI ESTER-TGAI		0 0 0 2 2 2		Yes Yes Yes	12 Months 12 Months 12 Months
82-3 - 90-Day Dermal	ACID-TGAI AMINE-TGAI ESTER-TGAI		0 0 0 2 2 2		No (8) No (8) No (8)	
82-4 - 90-Day Inhalation:	ACID-TGAI AMINE-TGAI ESTER-TGAI		0 0 0 Z Z Z		No (8) No (8) No (8)	
82-5 - 90-Day Neurotoxicity:	ACID-TGAI AMINE-TGAI ESTER-TGAI		0 0 0 2 Z Z		No (9) No (9) No (9)	
CHRONIC TESTING						
83-1 - Chronic Toxicity, 2 species: - Rodent, and	ACID-TGAI AMINE-TGAI ESTER-TGAI		Yes No No	00160876	No Reserved (10, 11) Reserved (10, 11)	
- Non-rodent (Dog)	ACID-TGAI AMINE-TGAI ESTER-TGAI		0 0 0 2 N N		Yes (11) Reserved (10, 11) Reserved (10, 11)	50 Months

TABLE A
GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS

Data Requirement	Test Substance	Use Patterns	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.340 Toxicology - Continued						
83-2 - Oncogenicity, 2 species: - Rat, and	ACID-TGAI AMINE-TGAI ESTER-TGAI		Partially No No	00160876	Reserved (12) Reserved (10) (Reserved (10)	
- Mouse	ACID-TGAI AMINE-TGAI ESTER-TGAI		Partially No No	40061801	Reserved (12) Reserved (10) (Reserved (10)	
83-3 - Teratcogenicity, 2 species: - Rat, and	ACID-TGAI AMINE-TGAI ESTER-TGAI		Yes No No	00130407, 00130707	No Yes Yes	15 Months 15 Months
- Rabbit	ACID-TGAI AMINE-TGAI ESTER-TGAI		0 0 0 0 0 0		Yes Yes Yes	15 Months 15 Months 15 Months
83-4 - Reproduction - Rat 2-generation	ACID-TGAI AMINE-TGAI ESTER-TGAI		Yes No	00150557	Reserved (13) Reserved (13) Reserved (13)	

TABLE A
GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS

Data Requirement	Test Substance	Use Patterns	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.340 Toxicology - Continued			·		·	
MUTAGENICITY TESTING					•	
84-2 - Gene Mutation	ACID-TGAI		8 S		Yes	9 Months
	ESTER-TGAI		0 0 2 Z		Yes	9 Months
84-2 - Structural Chromosomal	ACID-TGAI		o N		Yes	12 Months
Aberration	AMINE-TGAI ESTER-TGAI		No No		Yes	12 Months 12 Months
84-4 - Other Mechanisms of Mutagenicity	ACID-TGAI AMINE-TGAI ESTER-TGAI		9 9 S		Yes Yes	12 Months 12 Months 12 Months
SPECIAL TESTING					!	
85-1 - General Metabolism	ACID-TGAI		8 S		Yes	24 Months
	ESTER-TGAI		8		Yes	24 Months
81-X - Neurotoxicity (dermal)	ACID-TGAI AMINE-TGAI		N N		Yes (14) Yes (14)	12 Months
	ESTER-TGAI		o N		Yes (14)	12 Months

TABLE A
GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS

Data Requirement	Test Substance	Use Patterns	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.540 Plant Protection						
121-1 - TARGET AREA PHYTOTOXICITY	TEP	A,B,C,D,F,G	o Z		No (2)	
NONTARGET AREA PHYTOTOXICITY						
TIER I						
122-1 - Seed Germination	TGAI	A,B,C,D,G	No		No (3)	
Securing Emergence 122-1 - Vegetative Vigor 122-2 - Aquatic Plant Growth	TGAI TGAI	A,B,C,D,G A,B,C,D,G	0 0 V		No (3) No (3)	
TIER II						
123-1A - Seed Germination	TGAI	A,B,C,D,G	No		Yes	9 Months
Seeding Emergence 123-1B - Vegetative Vigor 123-2 - Aquatic Plant Growth	TGAI TGAI	A,B,C,D,G A,B,C,D,G	N N O		Yes Yes (4)	9 Months 9 Months

GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS TABLE A

Data Requirement	\$158.540 Plant Protection - Cont.	TIER III	124-1 - Terrestrial Field 124-2 - Aquatic Field
Test Substance			TEP
Use Patterns			A,B,C,D,G A,B,C,D
Does EPA Have Data to Satisfy This Requirement?			o o
Bibliographic Citation			
Must Additional Data be Submitted?	· ·		Reserved (5) Reserved (5)
Timeframe for Submission (1)			

GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS TABLE A

Data Requirement	Test Substance	Use Patterns	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.390 Reentry Protection						
132-1 - Foliar Dissipation	TEP	A,B	No		No (3)	
132-1 - Soil Dissipation	TEP	∢	No		No (3)	
133-3 - Dermal Exposure	TEP	A,B	N <sub>o</sub>		No (3)	
133-4 - Inhalation Exposure	TEP	A,B	No		No (3)	
\$158.440 Spray Drift						
201-1 - Droplet Size	TEP	A,B,C,D,G	No		Yes (4)	12 Months
202-1 - Drift Field	TEP	A,B,C,D,G	No		Yes (4)	24 Months

TABLE A
GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS

	Test Substance	Use Patterns	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.290 Environmental Fate						
DEGRADATION STUDIES-LAB						
161-1 - Hydrolysis	TGAI or PAIRA	A,B,C,D,G	No		Yes	9 Months
PHOTODEGRADATION						
161-2 - In Water	TGAI or PAIRA	A,B,C,D,G	ON :		Yes	9 Months
161-3 - On Soil 161-4 - In Air	IGAI or PAIRA TGAI or PAIRA	A,G	0 0 Z Z		Yes Yes	9 Months 9 Months
METABOLISM STUDIES-LAB						
161-1 - Aerobic Soil	TGAI or PAIRA	A,B,G	Partially	00116625	Yes (3)	27 Months
162-2 - Anaerobic Soil	TGAI or PAIRA	4	No		Yes	27 Months
162-3 - Anaerobic Aquatic 162-4 - Aerobic Aquatic	TGAI or PAIRA TGAI or PAIRA	C,D,G C,D	o o		Yes Yes	27 Months 27 Months
MOBILITY STUDIES						
163-1 - Leaching and	TGAI or PAIRA	A,B,C,D,G	Partially	00057313	Yes (4)	12 Months
Adsorption/Desorption 163-2 - Volatility (Lab) 163-3 - Volatility (Field)	TEP	<b>4</b> 4	o o	00112937	Yes	12 Months 15 Months

GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS **TABLE A** 

Data Requirement	Test Substance	Use Patterns	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
15.290 Environmental Fate Cont.						
DISSIPATION STUDIES - FIELD						
164-1 - Soil	TEP	A,B	o <sub>N</sub>		Yes	27 Months
164-2 - Aquatic (Sediment)	TEP	C,D,G	No		Yes	27 Months
164-3 - Forestry	TEP	ഇ	No		Yes	27 Months
164-4 - Combination and Tank Mixes	TEP	•	No		No (5)	
164-5 - Soil, Long-term	TEP	A,C	S <sub>O</sub>		Reserved (6)	
ACCUMULATION STUDIES						
165-1 - Rotational Crops (Confined)	PAIRA	A,C			Yes	39 Months
165-2 - Rotational Crops (Field)	TEP	A,C	S S		Reserved (7)	
165-3 - Irrigated Crops	TEP	C,D			Yes	39 Months
165-4 - In Fish	TGAI or PAIRA	A,B,C,D,G	Partially	00110675	Yes (8)	12 Months
165-5 - In Aquatic Non-Target Organisms	TEP	D'C		00110675	Yes (8)	12 Months

TABLE A
GENERIC DATA REQUIREMENTS FOR 2,4-DICHLOROPHENOXYACETIC ACID AND INORGANIC SALTS (2,4-D acid); AMINES AND ESTERS

Data Requirement	Test Substance	Use	Does EPA Have Data to Satisfy This Requirement?	Bibliographic Citation	Must Additional Data be Submitted?	Timeframe for Submission (1)
\$158.240 Residue Chemistry						
171-4A - Nature of the residue	PAIRA		Partially	00004666, 00004667 00004669, 00004675 00004676, 00004677 00004682, 00004683 00004689, 00004683 00004698, 00004693 00004715, 00004639 00004214, 00074215 00004216, 00074217 00102675, 00102676 00102679, 00102717	Yes (2)	18 Months
171-4B - Nature of the Residue (Metabolism) - Livestock	PAIRA and plant metabolites		Partially	40600202 00004705, 000068891	Yes (3,4)	18 Months

### TABLE B

# UNACCEPTABLE STUDIES SUBMITTED FOR 2.4-D ACID 2.4-D DMA SALT, 2.4-D 2-EH ESTER

(Account for appx. 80% of total 2,4-D products)

	(Account for appx. 80% of total 2,4-D products)
2.4-D Acid	
72-2a	Invertebrate Toxicity: (1 study was found unacceptable; guideline requirement is now satisfied)
72-3b	Estuarine/Marine Tox mollusk: 2 studies were found unacceptable; requirement has not been satisfied)
72-4a	Early lifestage - fish: 1 study found unacceptable; guideline requirement has since been satisfied with acceptable study.
81-5	Primary Dermal Irritation: 2 studies found unacceptable; guideline has been satisfied.
84-2b	Structural Chromosomal Aberration: 2 studies unacceptable; guideline has not been satisfied - study is in review.
84-4	Other Genotoxic Effects: 1 study unacceptable; guideline has been satisfied.
162-3	Anaerobic Aquatic Metabolism: 1 study unacceptable; repeat study being conducted.
2,4-D Dimet	nylamine Salt
71-2a	Acute Avian Dietary - Quail: 1 study unacceptable; guideline has been satisfied.
71-2b	Acute Avian Dietary - Mallard: 1 study unacceptable; another in review
83-3a	Developmental Tox Rat: 1 study unacceptable; guideline not satisfied
84-2b	Structural Chrom. Aberration: 1 study unacceptable; guideline has been satisfied.
84-4	Other Genotoxic Effects: 2 studies unacceptable; guideline now satisfied.
123-2	Aquatic Plant Growth: 1 study unacceptable, 3 acceptable; study in review (Guideline requirement is not satisfied)

Nature of the Residue (Plant Metabolism): Apple study unacceptable

171-4a

## 2.4-D 2-Ethylhexyl Ester

72-1a	Fish Toxicity - bluegill: 2 studies unacceptable; repeat study due 1/93
72-1c	Fish Tox rainbow trout: 1 study unacceptable; guideline has been satisfied.
72-2a	Invertebrate Toxicity: 1 study unacceptable; guideline has been satisfied.
81-3	Acute Inhalation Tox Rat: 1 unacceptable study; repeat study due 1/93
82-1a	90-day feeding - Rodent: 1 study unacceptable; requirement has been satisfied.
84-4	Other Genotoxic Effects: 1 study unacceptable; requirement has been satisfied.
85-1	General Metabolism: 1 study unacceptable; requirement not satisfied.
171-4a	Nature of the Residue (Plant Metabolism): 1 study unacceptable; 1 study in review.

# Appendix 3 2,4-D Exposure Reduction Agreement

# AGREEMENT on EXPOSURE REDUCTION MEASURES for 2,4-D LABELS Summary--October 1992

The agreement will be effected through the amendment of registrations of technical and manufacturing-use products containing 2,4-D acetic acid or any derivative of the acid. In addition to requiring new exposure reduction measures on product labels, the agreement also includes provisions for the implementation of a 2,4-D user education program on exposure reduction and for revised deadlines for submitting health and safety data required by the Agency. Where more restrictive requirements currently appear on product labels (because of multiple active ingredients, existing maximum application rates, etc.), the more restrictive requirements will apply.

Products containing the following active ingredients are covered by the exposure reduction measures:

2,4-Dichlorophenoxyacetic acid (2,4-D) and its derivatives:

Sodium salt of 2,4-D or sodium 2,4-dichlorophenoxyacetate

Diethanolamine salt of 2,4-D or diethanolamine 2,4-dichlorophenoxyacetate

Dimethylamine salt of 2,4-D or dimethylamine 2,4-dichlorophenoxyacetate

Isopropylamine salt of 2,4-D or isopropylamine 2,4-dichlorophenoxyacetate

Triisopropanolamine salt of 2,4-D or triisopropanolamine 2,4-dichlorophenoxyacetate

2-Butoxyethyl ester of 2,4-D or butoxyethyl 2,4-dichlorophenoxyacetate

Isooctyl (2-ethylhexyl) ester of 2,4-D or acetic acid, (2,4-dichlorophenoxy)-, 2-ethylhexyl ester Isopropyl ester of 2,4-D or isopropyl 2,4-dichlorophenoxyacetate

### Protective Clothing

All users and mixers/loaders/applicators (M/L/As) must wear long-sleeved shirt, long pants, shoes, socks.

M/L/As of agricultural, industrial, and aquatic use products must also wear chemical-resistant gloves and face shield or safety glasses. Eye protection is not required for applicators in completely enclosed cabs or cockpits.

Users of turf liquid products with "WARNING" or "DANGER" signal words must also wear eye protection.

Users of turf liquid amine products must also wear rubber gloves.

Users of turf liquid ester, Na (sodium) salt, and acid products must also wear chemical-resistant gloves.

Persons who engage in open pouring of containers of over 1 gallon (and less than 5 gallons) in capacity must also wear coveralls or chemical-resistant apron.

### Mechanical Transfer Systems

"Probe and pump" systems must be used for transferring the contents of containers 5 gallons or more in capacity. Probe must be decontaminated before removal from an empty container.

### **Maximum Application Rates**

- 2 lbs. acid equivalent (ae) per acre per application for pasture and rangeland (except for hard-to-kill woody species)
- 4 lbs. ae per acre per application for forestry site preparation
- 2 lbs. ae per acre per application for turf

### Maximum Application Frequency

2 broadcast applications per year per site for turf

### Hygiene Statements

For agricultural, industrial, and aquatic uses:

"Wash hands, face and arms with soap and water as soon as possible after mixing, loading, or applying this product. Wash hands, face and arms with soap and water before eating, smoking, or drinking. Wash hands and arms before using toilet. After work, remove all clothing and shower using soap and water. Do not reuse clothing worn during the previous day's mixing and loading or application of this product without cleaning first. Clothing must be kept and washed separately from other household laundry. Remove saturated clothing as soon as possible and shower."

### For turf uses:

For granular products, "After using this product, remove clothing and launder separately before reuse, and promptly and thoroughly wash hands and exposed skin with soap and water."

For liquid products, "After using this product, rinse gloves before removing, remove clothing and launder separately before reuse, and promptly and thoroughly wash hands and exposed skin with soap and water. Remove saturated clothing as soon as possible and shower."

### Restricted Entry Interval

Agricultural uses (including sod farms) and forestry uses are covered by the provisions of the Worker Protection Standard.

For turf: "Do not allow people (other than applicator) or pets on treatment area during application. Do not enter treated areas until spray has dried or dust has settled."

### Effective Dates

Any consumer 2,4-D product formulated after October 23, 1993 or sold by the registrant after April 15, 1994 for use on sites other than turf (including sod farms) will have the new exposure reduction measures on the label.

Any consumer 2,4-D product formulated after June 15, 1994 or sold by the registrant after January 1, 1995 for use on residential or other turf sites (excluding sod farms) will have the new exposure reduction measures on the label.

### For more information, contact:

Jill Bloom (703) 308-8019 or Rich Dumas (703) 308-8015 Special Review and Reregistration Division (H7508W) U.S. Environmental Protection Agency 401 M St., S.W. Washington, DC 20460