# Rights of Way Sensitive Area Materials List

<table>
<thead>
<tr>
<th>Active Ingredient</th>
<th>Product Names (EPA #)</th>
<th>Registrant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Glyphosate</strong></td>
<td><strong>Round Up Pro (524-475)</strong></td>
<td>Monsanto</td>
</tr>
<tr>
<td><strong>Lowest Labeled Rate for all Glyphosate products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Aquaneat Aquatic Herbicide (228-365)</strong></td>
<td>Dow AgroSciences</td>
</tr>
<tr>
<td></td>
<td><strong>Razor (228-366)</strong></td>
<td>Dow AgroSciences</td>
</tr>
<tr>
<td></td>
<td><strong>Razor-Pro (228-366)</strong></td>
<td>Dow AgroSciences</td>
</tr>
<tr>
<td></td>
<td><strong>Nu Farm Americas</strong></td>
<td>Dow AgroSciences</td>
</tr>
<tr>
<td>While Accord Concentrate, Rodeo, Glyphosate VMF and Aquaneat all have aquatic uses, approval for their use as sensitive materials does NOT mean that they can be used for aquatic weed control, or directly applied to water, as part of a rights of way management program. Products are subject to the no-spray and limited spray provisions of 333 CMR 11.04.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Metsulfuron Methyl</strong></td>
<td><strong>Escort XP (352-439)</strong></td>
<td>EI Dupont</td>
</tr>
<tr>
<td><strong>Lowest Labeled Rate for all Metsulfuron Methyl Products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sulfometuron Methyl</strong></td>
<td><strong>Oust XP (352-601)</strong></td>
<td>EI Dupont</td>
</tr>
<tr>
<td><strong>Lowest Labeled Rate for all Sulfometuron-Methyl Products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Metsulfuron Methyl</strong></td>
<td><strong>Oust Extra (352-622)</strong></td>
<td>EI Dupont</td>
</tr>
<tr>
<td><strong>Sulfometuron Methyl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Lowest Labeled Rate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ammonium Salt of Fosamine</strong></td>
<td><strong>Krenite S (352-395)</strong></td>
<td>EI Dupont</td>
</tr>
<tr>
<td><strong>Lowest Labeled Rate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Imazapyr</strong></td>
<td><strong>Arsenal (241-346)</strong></td>
<td>BASF</td>
</tr>
<tr>
<td><strong>3 pints/acre every 3rd year OR</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2 pints/acre every other year for all Imazapyr Products</strong></td>
<td><strong>Arsenal Powerline (241-431)</strong></td>
<td>BASF</td>
</tr>
<tr>
<td><strong>for</strong></td>
<td><strong>Arsenal Railroad Herbicide (241-273)</strong></td>
<td>BASF</td>
</tr>
<tr>
<td><strong>Polaris AC Complete Herbicide (228-570)</strong></td>
<td><strong>Polaris Herbicide (228-534)</strong></td>
<td>Nu Farm Americas</td>
</tr>
<tr>
<td><strong>Paclobutrazol</strong></td>
<td><strong>Garlon 4 (62719-40)</strong></td>
<td>Dow AgroSciences</td>
</tr>
<tr>
<td><strong>Lowest Labeled Rate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>The lowest of the following rates:</strong></td>
<td><strong>Garlon 4 Ultra (62719-527)</strong></td>
<td>Dow AgroSciences</td>
</tr>
<tr>
<td>1. Between 10 feet and 50 feet of the resource: Lowest labeled rate* or 0.5 pints per acre</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Between 50 feet and the boundary of the limited spray zone: Lowest labeled rate* or 3 pints per acre</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cambistat (74779-3)</strong></td>
<td><strong>Rainbow Tree care</strong></td>
<td>Nu Farm Americas</td>
</tr>
</tbody>
</table>

*Lowest labeled rate* the minimum labeled rate of the pesticide product for the appropriate site, pest and application method

**Disclaimer**

The Massachusetts Department of Agricultural Resources (MDAR) makes no endorsement of any companies, organizations, persons, products, trade or brand names referenced in this Rights of Way Sensitive Area Materials List ("the list"). Active Ingredients on the list are reviewed pursuant to a Cooperative Agreement between MDAR and the Massachusetts Department of Environmental Protection. Only environmental fate and toxicological data, including eco-toxicological data, are reviewed when evaluating an active ingredients suitability for inclusion on the list. Inclusion on the list does not represent any endorsement by MDAR as to the efficacy of the active ingredient for rights-of-way vegetation management.
GLYPHOSATE

In addition to the review that is presented below, a comprehensive review available from USDA Forest Service provides information that incorporates more recent studies and data. The US Forest Service risk assessment report is available at: http://www.fs.fed.us/foresthealth/pesticide/risk.shtml

Review conducted by MDAR and MassDEP for use in Sensitive Areas of Rights-of-Way in Massachusetts

Common Trade Name(s): Roundup, Glyphosate VMF Round Up Pro, Rodeo, Accord, Accord Concentrate,

Chemical Name: N—(phosphonomethyl )glycine—isopropylamine salt
CAS No.: 1071-83-6

GENERAL INFORMATION
Glyphosate, n-phosphonomethyl glycine, is a systemic, broad spectrum herbicide effective against most plant species, including deep rooted perennial species, annual and biennial species of grasses, sedges, and broadleafed weeds. The major pathway for uptake in plants is through the foliage, however, some root uptake may occur. The presence of surfactants and humidity increases the rate of absorption of glyphosate by plants (15).

Foliarly applied glyphosate is readily absorbed and translocated from treated areas to untreated shoot regions. The mechanism of herbicidal action for glyphosate is believed to be inhibition of amino acid biosynthesis resulting in a reduction of protein synthesis and inhibition of growth (10, 15, 101).

Glyphosate is generally formulated as the isopropylamine salt in aqueous solution (122). Of the three products containing glyphosate considered here, Roundup is sold with a surfactant and Rodeo and Accord are mixed with surfactants prior to use (15). Glyphosate has been reviewed by US Forest Service (15), FAO (122), and EPA 00W (51).

ENVIRONMENTAL FATE

Mobility
Glyphosate is relatively immobile in most soil environments as a result of its strong adsorption to soil particles. Adsorption to soil particles and organic matter begins almost immediately after application. Binding occurs with particular rapidity to clays and organic matter (15). Clays and organic matter saturated with iron and aluminum (such as in the Northeast) tend to absorb more glyphosate than those saturated with sodium or calcium. The soil phosphate level is the main determinant of the amount of glyphosate adsorbed to soil particles. Soils which are low in phosphates will adsorb higher levels of glyphosate (14, 15).

Glyphosate is classified as immobile by the Helling and Turner classification system. In soil column leaching studies using aged (1 month) Glyphosate, leaching of glyphosate was said to be insignificant after 0.5 inches of water per day for 45 days (14).
Persistence
It has been reported that glyphosate dissipates relatively rapidly when applied to most soils (14). However, studies indicate that the soil half-life is variable and dependent upon soil factors. The half-life of glyphosate in greenhouse studies when applied to silty clay loam, silt loam, and sandy loam at rates of 4 and 8 ppm was 3, 27 and 130 days respectively, independent of application rate (14). An average half-life of 2 months has been reported in field studies for 11 soils (15).

Glyphosate is mainly degraded biologically by soil micro-organisms and has a minimal effect on soil microflora (15). In the soil environment, glyphosate is resistant to chemical degradation such as hydrolysis and is stable to sunlight (15). The primary metabolite of glyphosate is aminomethyl phosphonic acid (AMPA) which has a slower degradation rate than glyphosate (15). The persistence of AMPA is reported to be longer than glyphosate, possibly due to tighter binding to soil (14). No data are available on the toxicity of this compound.

Glyphosate degradation by microorganisms has been widely tested in a variety of field and laboratory studies. Soil characteristics used in these studies have included organic contents, soil types and pHs similar to those that occur in Massachusetts (117).

Glyphosate degradation rates vary considerably across a wide variety of soil types. The rate of degradation is correlated with microbial activity of the soils and does not appear to be largely dependent on soil pH or organic content (117). While degradation rates are likely temperature dependent, most reviews of studies do not report or discuss the dependence of degradation rate on temperature. Mueller et al. (1981 cited in 117) noted that glyphosate degraded in Finnish agricultural soils (loam and fine silt soils) over the winter months; a fact which indicates that degradation would likely take place in similar soils in the cool Massachusetts climate. Glyphosate half-lives for laboratory experiments on sandy loam and loamy sand, which are common in Massachusetts, range up to 175 days (117). The generalizations noted for the body of available results are sufficiently robust to incorporate conditions and results applicable to glyphosate use in Massachusetts.

TOXICITY REVIEW

Acute (Mammalian)
Glyphosate has reported oral LD50s of 4,320 and 5,600 mg/kg in male and female rats (15,4). The oral LD50s of the two major glyphosate products Rodeo and Roundup are 5,000 and 5,400 mg/kg in the rat (15).

A dermal LD50 of 7,940 mg/kg has been determined in rabbits (15,4). There are reports of mild dermal irritation in rabbits (6), moderate eye irritation in rabbits (7), and possible phototoxicity in humans (9). The product involved in the phototoxicity study was Tumbleweed marketed by Murphy’s Limited UK (9). Maibach (1986) investigated the irritant and the photo irritant responses in individuals exposed to Roundup (41% glyphosate, water, and surfactant); Pinesol liquid, Johnson Baby Shampoo, and Ivory Liquid dishwashing detergent. The conclusion drawn was that glyphosate has less irritant potential than the Pinesol or the Ivory dishwashing liquid (120).

Metabolism
Elimination of glyphosate is rapid and very little of the material is metabolized (6,106).
Subchronic/Chronic Studies (Mammalian)
In subchronic tests, glyphosate was administered in the diet to dogs and rats at 200, 600, and 2,000 ppm for 90 days. A variety of toxicological endpoints were evaluated with no significant abnormalities reported (15,10).

In other subchronic tests, rats received 0, 1,000, 5,000, or 20,000 ppm (57, 286, 1143 mg/kg) in the diet for 3 months. The no observable adverse effect level (NOAEL) was 20,000 ppm (1,143 mg/kg) (115). In the one year oral dog study, dogs received 20, 100, and 500 mg/kg/day. The no observable effect level (NOEL) was 500 mg/kg (116).
Oncogenicity Studies
Several chronic carcinogenicity studies have been reported for glyphosate including an 18 month, mouse study; and a two year rat study. In the rat study, the animals received 0, 30, 100 or 300 ppm in their diet for 2 years. EPA has determined that the doses in the rat study do not reach the maximum tolerated dose (112) and replacement studies are underway with a high dose of 20,000 ppm (123). The mice received 1000, 5000 or 30,000 ppm for 18 months in their diets. These studies were non-positive (112,109). There was a non-statistically significant increase in a rare renal tumor (renal tubular adenoma (benign) in male mice (109). The rat chronic study needs to be redone with a high dose to fill a partial data gap (112). The EPA weight of evidence classification would be D: not classified (51).

Mutagenicity Testing
Glyphosate has been tested in many short term mutagenicity tests. These include 7 bacterial (including Salmonella typhimurim and B. subtilis) and 1 yeast strain Sacchomyces cerevisiae as well as a mouse dominant lethal test and sister chromatid exchange. The microbial tests were negative up to 2,000 mg/plate (15), as were the mouse dominant lethal and the Chinese hamster ovary cell tests. EPA considers the mutagenicity requirements for glyphosate to be complete in the Guidance for the Registration of Pesticide Products containing glyphosate (112).

The developmental studies that have been done using glyphosate include teratogenicity studies in the rat and rabbit, three generation reproduction studies in the rat, and a reproduction study in the deer mouse. (15)

Rats were exposed to levels of up to 3,500 mg/kg/d in one rat teratology study. There were no teratogenic effects at 3,500 mg/kg/d and the fetotoxicity NOEL was 1,000 mg/kg/d. In the rabbit study a fetotoxicity NOEL was determined at 175 mg/kg/d and no teratogenic effects were observed at 10 or 30 mg/kg/d in one study and 350 mg/kg/d in the other study (15). No effects were observed in the deer mouse collected from conifer forest sprayed at 2 lbs active ingredient per acre (15).

Tolerances & Guidelines
EPA has established tolerances for glyphosate residues in at least 75 agricultural products ranging from 0.1 ppm (most vegetables) to 200 ppm for animal feed commodities such as alfalfa (8).

U.S. EPA Office of Drinking Water has released draft Health Advisories for Glyphosate of 17.50 mg/L (ten day) and 0.70 mg/L (Lifetime)(51).

Avian
Two types of avian toxicity studies have been done with glyphosate: ingestion in adults and exposure of the eggs. The species used in the ingestion studies were the mallard duck, bobwhite quail, and the adult hen (chickens). The 8 day feeding LC50s in the mallard and bobwhite are both greater than 4,640 ppm. In the hen study, 1,250 mg/kg was administered twice daily for 3 days resulting in a total dose of 15,000 mg/kg. No behavioral or microscopic changes were observed (15).

Invertebrates
A variety of invertebrates (mostly arthropods) and microorganisms from freshwater, marine, and terrestrial ecosystems have been studied for acute toxic effects of technical glyphosate as well as formulated Roundup. The increased toxicity of Roundup compared with technical glyphosate in some studies indicates that it is the surfactant (MONO 818) in Roundup that is the primary toxic agent (117). Acute toxicity information may be summarized as follows:

Glyphosate (technical): Acute toxicity ranges from a 48 hr EC50 for midge larvae of 55 mg/L to a 96 hr TL50 for the fiddler crab of 934 mg/L (15).

Roundup: Acute toxicity ranges from a 48 hr EC50 for Daphnia of 3 mg/L to a 95 hr LC50 for crayfish of 1000 mg/L (15).
Among the insects tested, the LD50 for honeybees was 100 mg/bee 48 hours after either ingestion, or topical application of technical glyphosate and Roundup. This level of experimental exposure is considerably in excess of exposure levels that would occur during normal field applications (15).

Aquatic Species (Fish) Technical glyphosate and the formulation Roundup have been tested on various fish species. Roundup is more toxic than glyphosate, and it is the surfactant that is considered to be the primary toxic agent in Roundup:

Glyphosate (technical):
Acute 96 hr LC5Os range from 24 mg/L for bluegill (Dynamic test) to 168 mg/L for the harlequin fish (15).

Roundup: Acute lethal toxicity values range from a 96 hr LC5O for the fathead minnow of 2.3 mg/L to a 96 hr TL5O for rainbow trout of 48 mg/L (15).

Tests with Roundup show that the egg stage is the least sensitive fish life stage. The toxicity increases as the fish enter the sac fry and early swim up stages.

Higher test temperatures increased the toxicity of Roundup to fish, as did higher pH (up to pH 7.5). Above pH 7.5, no change in toxicity is observed.

Glyphosate alone is considered to be only slightly acutely toxic to fish species (LC5Os greater than 10 mg/L), whereas Roundup is considered to be toxic to some species of fish, having LC5Os generally lower than 10 mg/L (15,118).

SUMMARY
Glyphosate when used as recommended by the manufacturer, is unlikely to enter watercourses through run-off or leaching following terrestrial application (117). Toxic levels are therefore unlikely to occur in water bodies with normal application rates and practices (118).

Glyphosate has oral LD5Os of 4,320 and 5,600 in male and female rats respectively. The elimination is rapid and very little of it is metabolized. The NOAEL in rats was 20,000 ppm and 500 mg/kg/d in dogs. No teratogenic effect was observed at doses up to 3,500 mg/kg/d and the fetotoxicity NOELS were 1,000 mg/kg/d in the rat and 175 mg/kg/d in the rabbit.

The evidence of oncogenicity in animals is judged as insufficient at this time to permit classification of the carcinogenic potential of glyphosate. The compound is not mutagenic.

REFERENCES


9. Dept. of Justice - Drug Enforcement Administration Memo dated September 26, 1985


51. Office of Drinking Water Health Advisories, USEPA


115. Monsanto-Memo-Rat Feeding Study 3 Month.

116. Monsanto-Memo-RE: Day 1 year oral


118. Non-Target Impacts of the Herbicide Glyphosate Mammal Pest Management, LTD.


123. Personal communication with Bill Heydens of Monsanto 2/16/89
IMAZAPYR

In addition to the review that is presented below, a comprehensive review available from USDA Forest Service provides information that incorporates more recent studies and data. The US Forest Service risk assessment report is available at: [http://www.fs.fed.us/foresthealth/pesticide/risk.shtml](http://www.fs.fed.us/foresthealth/pesticide/risk.shtml)

Review conducted by MDAR and MassDEP for use in Sensitive Areas of Rights-of-Way in Massachusetts

Common Trade Name(s): Arsenal

Chemical Name: Imazapyr!

\[ 2-(4\text{-isopropyl}-4\text{-methyl}-5\text{-oxy}-2\text{-imidazolin}-2\text{-yl}) \]
\[ \text{nicotinic acid with isopropyl amine (2)} \]

CAS No.: 81510-83-0

GENERAL INFORMATION

Imazapyr is effective against and provides residual control of a wide variety of annual and perennial weeds, deciduous trees, vines and brambles in non—cropland situations. It also provides residual control and may be applied either pre or postemergence. Postemergence is the preferred method especially for the control of perennial species. Imazapyr is readily absorbed by the foliage and from soil by the root systems. Imazapyr kills plants by inhibiting the production of an enzyme, required in the biosynthesis of certain amino acids, which is unique to plants (10, 100).

ENVIRONMENTAL FATE

Mobility

There are few studies which have investigated the mobility of Imazapyr in soil, but available reports indicate that Imazapyr does not leach and is strongly absorbed to soil (100). Imazapyr has a high water solubility (1 — 1.5%) which could generally indicate a high leaching potential, but as with other organic acids Imazapyr is much less mobile than would normally be expected (100). No soil partition coefficients have been reported, but they may be expected to be quite high (100).

One field study investigated Imazapyr mobility in a sandy loam soil (0.9% organic matter, 8.0% clay; 38.8% silt). Imazapyr did not leach below the 18—21 inch layer after 634 days and 49.6 inches of rain. The levels found below the 12 inch layer were just above the 5 ppb detection limit. In addition, this study investigated the off—target mobility of Imazapyr and found no residues further than 3 inches from the sprayed area after 1 year (102).
Although low levels of Imazapyr did move to the 18 to 21 inch layer this was only after nearly 2 years and fifty inches of rain. This indicates that imazapyr is relatively non-mobile and does not leach through the soil profile. Imazapyr remains near the soil surface and heavy precipitation may cause some off target movement from surface erosion of treated soils.

**Persistence**

The main route of Imazapyr degradation is photolysis. In a study of photodegradation in water, the half—life of Imazapyr was calculated as 3.7, 5.3 and 2.5 days in distilled water, pH 5 and pH 9 buffers respectively (101). A soil photolysis study for Arsenal on sandy loam calculated a half—life of 149 days (101).

Studies have investigated the persistence of Imazapyr in soil under aerobic and anaerobic conditions. The half-life of Imazapyr in soil has been reported as varying from 3 months to 2 years (100). A laboratory study found the half-life to be 17 months (101). Detectable residues were found in a field study in all soil layers to 21 inches at 634 days (102). Vegetation was sprayed with radio-labelled Imazapyr at a rate of 1 lb. a.i./acre. The soil was a sandy loam (0.9% organic matter) which received 49.6 inches of rain during 634 days. The highest level of radioactivity (0.234 ppm Imazapyr) was found in the top 3 inches of soil at 231 days after application and there were detectable levels in the 9-12 inch layer. The concentrations in the top layer increased steadily from day 4 to 231 when they reached their maximum (0.234 ppm) and then declined. At day 634 the level in the top layer (0-3 inch) was 0.104 ppm (102). These data indicate that Imazapyr is persistent in soil and, most importantly, that Imazapyr is translocated within plants from the plant shoots back to the roots and released back into soil. Very little of the Imazapyr actually reached the soil during application. The soil residues may be due to the decay of plant material containing Imazapyr in the soil (102).

**TOXICITY REVIEW**

**Acute (Mammalian)**

The acute oral LD50 in both male and female rats was greater than 5000 mg/kg using technical Imazapyr. The acute dermal LD50 in male and female rabbits was greater than 2000 mg/kg. The compound was irritating to the rabbit eye but recovery was noted 7 days after application of 100 mg of the test substance. It was classified as mildly irritating to the rabbit skin following application of 0.5 grams of the material on abraded or intact skin (103).

Arsenal product formulation was tested in a similar battery of tests. The rat oral LD50 value was greater than 5000 mg/kg and the rabbit dermal LD50 was greater than 2148 mg/kg. The irritation was observed following installation of 0.5 ml of the test substance in the skin study and 0.1 ml in the eye study (104).

Technical Imazapyr was administered to rats as an aerosol for four hours at a concentration of 5.1 mg/L. There were ten rats per sex and the animals were observed for 14 days after treatment before they were sacrificed. Slight nasal discharge was seen in all rats on day one but disappeared on day two (105).

The inhalation LC50 is greater than 5.0 mg/L for both the formulation and the technical product (105,106). Technical Imazapyr was applied dermally at the following dosages: 0, 100, 200 and 400 mg/kg/day (109). Arsenal was used at 0, 25, 50 and 100% of the formulated solution in sterile saline. Each dose group consisted of 10 male and 10 female rabbits and the test substance was applied to either intact or abraded skin and occluded for 6 hours each day.

The result of the dermal studies with Imazapyr as well as Arsenal were non remarkable with regard to body weights, food consumption, hematology, serum chemistry, clinical observations, necropsy observations and histopathology. It was noted that Arsenal, undiluted, was locally irritating (109).

**Subchronic and Chronic Studies (Mammalian)**
In the subchronic tests a NOEL for systemic toxicity with dermal administration in rabbits was 400 mg/kg/d (2,109). After dietary administration for 13 weeks in the rat, there was no effect at 10,000 ppm (571. mg/kg/d) which was the highest dose tested (141).

A bioassay is currently underway to evaluate the potential oncogenicity of technical Imazapyr. Groups of 65 rats per sex per dose group have received 0, 1000, 5000 or 10,000 ppm in the diet. Hematology, clinical chemistry and urinalysis tests were conducted at 3, 6 and 12 months and will also be done at 18 months and at study termination. At the 12 month sacrifice the only effect noted was a slight increase in mean food consumption in all treated female groups. Most of the increases were statistically significant, but they did not always exhibit a dose response. The oncogenicity test is due to be submitted to the EPA in the spring of 1989 (115).

**Oncogenicity Studies**

Chronic bioassays as discussed in the subchronic/chronic section are underway.

**Mutagenicity Testing**

Five different bacterial strains of *Salmonella typhimurium* (TA1535, TA98, TA100, TA1537, and TA1538) and one of *Escherichia coli* (WP-2 uvrA-) were used to evaluate the mutagenicity of Imazapyr. It is unclear whether the compound used was technical or formulated Imazapyr. Dose levels up to 5000 micrograms/plate were used and each strain was evaluated both in the presence or absence of PCB—induced rat liver 5—9 microsomes. Negative results were noted in all assays. The six tester strains were designed to detect either base-pair substitutions or frameshift mutations (113).

**Developmental Studies (Mammalian)**

Two teratology studies have been done and both of these studies evaluated technical Imazapyr. One study used rats as the test species and the other utilized rabbits (111,112).

Pregnant rats received dosages of 0, 100, 300 or 1000 mg/kg/d of Imazapyr during days 6—15 of gestation. There were 22 rats in the control group and 24, 23 and 22 in the low, mid and high dose groups. All doses were administered orally by gavage. Salivation was noted only during the dosing period in 6 of the 22 females in the highest dose group (1000 mg/kg). No other adverse observations were noted in the treated dams (111). Fetal body weight and crown-rump length data for the treated groups were comparable to controls. Fetal development (external, skeletal and visceral) “revealed no aberrant structural changes which appeared to be the result of the exposure to Imazapyr” (111). The NOEL for maternal toxicity was 300 mg/kg and the NOEL for teratogenicity and fetotoxicity was 1000 mg/kg (116).

Four groups of 18 pregnant rabbits were exposed on days 6-18 of gestation to doses of 0, 25, 100, 400 mg/kg/d Imazapyr. There was no statistically significant difference between control and treated groups at any dose (112).

**Avian**

Acute oral LD50s of Imazapyr in bobwhite quail and mallard duck were 2150 mg/kg. The 8 day dietary LC50 in the bobwhite quail and mallard duck were greater than 5000 ppm (101).

**Invertebrates**

The dermal honey bee LD50 for Imazapyr is greater than 100 mg/bee (101). The LD50 (48 hr) was greater than 100 mg/L for the water flea (100).

**Aquatic**
The LC50s of Imazapyr in the rainbow trout, bluegill sunfish and channel catfish were greater than 100 mg/L (101).

SUMMARY
Imazapyr is a relatively immobile herbicide in the soil profile even when used in sandy and low organic content soils. It is also persistent in soils. The low mobility and persistence may result in off-target movement of Imazapyr from surface erosion of treated soils.

The atypical soil—plant flux characteristics of Imazapyr and delayed maximum soil concentrations indicate that repeated annual applications may result in build—up of Imazapyr in soil. Consequently, an interval is required to allow for the degradation of soil residues before a repeated application is made.

The oral LD50 of Imazapyr in rats is greater than 5000 mg/kg and the dermal LD5O is greater than 2000 mg/kg in rabbits. The oncogenicity bioassay is currently underway and the only effect reported in the interim study was an increase in food consumption in the treated females. No mutagenic effects were observed.

The acute oral LD5Os of Imazapyr and the Arsenal formulation are greater than 5000 mg/kg. In the subchronic 13 week rat study there was no effect observed at the highest dose tested 10,000 ppm. The oncogenicity study is currently underway.

REFERENCES

101. American Cyanamid Arsenal Herbicide Environmental and Toxicological Data Summary.


104. Acute Toxicology of AC 252,925 22.6% to Rats and Rabbits. American Cyanamid Company, A83-67.


108. Evaluation of the Sensitization Potential of AC 252,925 in Guinea Pigs. Toxicology Pathology Services, Inc. Study No. 186A—201-231-83.

110. Twenty—one Day Dermal Toxicity Study with AC 252,925 in Rabbits. Toxicology Pathology Services, Inc. Study No. 187B-230-83.

111. Teratology Study in Albino Rats with AC 243,997. ToxiGenics Study No. 450-1222.

112. Teratology Study in Albino Rabbits with Ac 243,997. ToxiGenics Study No. 450-1224.


METSULFURON METHYL

In addition to the review that is presented below, a comprehensive review available from USDA Forest Service provides information that incorporates more recent studies and data. The US Forest Service risk assessment report is available at: http://www.fs.fed.us/foresthealth/pesticide/risk.shtml

Review conducted by MDAR and MassDEP for use in Sensitive Areas of Rights-of-Way in Massachusetts

Common Trade Names: Escort, Escort XP (2)

Chemical Name: Methyl 2 E[(4-Methoxy—6-methyl-1,3,5-Triazifl—2-yl) aminolcarbonyl] amino] sulfonyl]benzoate] (9)

CAS NO.: 74223-64-6

GENERAL INFORMATION

Metsulfuron methyl is a sulfonyl urea herbicide initially registered by E.I. DuPont in 1986. It is a foliar herbicide registered for use on wheat and barley and non-cropland sites such as Right of Way (9).

ENVIRONMENTAL FATE

Mobility
Metsulfuron methyl is a relatively new herbicide. The studies reviewed here have been provided by the registrant, El DuPont.

The soil water partition coefficients (Kd) of Metsulfuron Methyl have been determined in four different soils: Cecil sand, Flanagan silt loam, Fallsington silt loam, and keyport silt loam. The Kd values range from 0.36 for Cecil sand to 1.40 for Flanagan silt loam, and Kom values ranged from 29 for Fallsington silt loam to 120 for Cecil sand (100). The values for Kd and Kom indicate that metsulfuron methyl is not adsorbed well to soil and that the organic content of the soil is not the only adsorption component. The silt and clay contents appear to influence adsorption, but there are probably other factors also involved.

The previous study also determined the Rf values for soil. Thin layer chromatography was performed on four soils for metsulfuron methyl. The Rf values ranged from 0.64 to 1.00; only one value was less than 0.90 (100). This result confirms the validity of the Kd values, indicating that metsulfuron methyl is mobile and that the organic matter content of the soil is a significant component of adsorption.

Metsulfuron methyl was applied to tops of 12 inch columns [containing four different soils], and eluted with 20 inches of water in 20 hours. Following the percolation of the total volume of water, 106% of the metsulfuron...
Methyl was eluted from the Fallsington sandy loam, 96% from the Flanagan silt loam, 81% for Keyport silt loam and 93% for Myakka sand (100). The breakthrough volumes for the Fallsington, Flangan, Keyport and Myakka soils were 6.5, 4.5, 6.9 and 5.8 inches of water respectively (101).

Metsulfuron methyl is relatively mobile in most soils, but will be retained longer in soils with higher percentages of organic matter.

Persistence
There are two studies which have reviewed the persistence of metsulfuron methyl in the soil. One study was conducted in the southern United States and the second was in the northern United States and Canada. The results of the studies indicate a somewhat contradictory picture of the persistence of metsulfuron methyl.

The soil half-lives in Delaware, North Carolina, Mississippi and Florida were 1 week, 4 weeks, 3 weeks and 1 week respectively following an application in mid to late summer (102). The results are varied and indicate that either climatic or soil factors determine the persistence. The climate is sufficiently similar to be able to discount that as a factor. However, both of the locations where the shortest half-lives were observed had the highest organic matter content in the soils. Furthermore, the half—lives correspond with the organic matter content.

The half—lives following spring applications were 4 and 56 weeks for two sites in Colorado, 6 weeks in North Dakota and 28 weeks in Idaho (103). In contrast to the southern United States study there does not appear to be any correlation with climatic or soil characteristics. There appears to be a slightly shorter half—life in acidic soils in the same location.

Metsulfuron methyl was also applied in the fall and the half-lives determined in two sites in Colorado, North Dakota and Idaho. These half—lives were 8 weeks, 12 weeks, 42 weeks and 28 weeks respectively. As was expected there were longer half—lives following fall applications in North Dakota (6 weeks vs. 42 weeks) however, in Idaho there was no change at all, which is unexpected.

In Canada following spring applications the reported half-lives were 10 weeks, 4 weeks, 4 weeks and 6 weeks for Alberta, 2 locations in Saskatchewan and Manitoba (103). One would expect longer half lives in Northern locations due to the effects of temperature on degradation rates. The results from Canada are generally shorter than those in the U.S. locations, which is unexpected.

Therefore, the half-life of Metsulfuron methyl in the soil is variable and dependent on the location. It is shorter when applied in the spring but appears independent of other environmental factors in most locations.

TOXICITY REVIEW

Acute (Mammalian)
The toxicology database for Metsulfuron methyl has been reviewed and accepted by the EPA (9). DuPont supplied excerpts from their monograph on Ally herbicide (112). Summaries of studies were supplied by DuPont for subchronic, chronic and reproductive studies.

Technical metsulfuron methyl has been tested in two acute oral LD50 studies in Crl:CD Rats. In the first study the LD50 was greater than 5,000 mg/kg and in the second it was greater than 25,000 mg/kg (the maximum feasible dose) (112). Clinical signs included salivation, chromodacryorrhea, stained face, stained perineal area and weight loss (112).

In a 10—dose subacute study using male rats, a single repeated dose of 3,400 mg/kg/day for 10 days over a 2 week period was administered. This was followed by a two week recovery period. No deaths occurred and slight weight loss was the only clinical sign observed. In addition, no gross or microscopic changes were observed (112). The dermal LD50 is greater than 2,000 mg/kg in male and female rabbits (112). Technical metsulfuron methyl caused mild erythema as a 40% solution in guinea pigs. There was no reaction observed at the 4% concentration. No response occurred when treated animals were challenged (112).

In rabbits, moderate areas of slight corneal clouding and severe to moderate conjunctivitis were observed in both washed and unwashed eyes following treatment with technical metsulfuron methyl. The unwashed eyes were
normal in 3 days and the washed eyes in 14 days (112).

**Metabolism**
Elimination of metsulfuron methyl in the rat is rapid, with 91% of a radioactive dose excreted over 96 hours (9). The routes of elimination were not specified within the report.

**Subchronic/Chronic (Mammalian)**
Ninety day feeding studies have been done with metsulfuron methyl in rats and mice. The rat study was done in conjunction with a one generation reproduction study (see Developmental Study Section). In this study rats received 0, 100, 1000, or 7500 ppm (0, 5.7, 57, 428 mg/kg/d) (a) in their diets. Effects observed at the high dose were: a decrease in body weight and an increase in total serum protein in the females, and a decrease in liver weight and a decrease in cytoplasmic clearing of hepatocytes in the males the NOEL in this study was 1000 ppm (104).

The 90 day mouse study was done in conjunction with the 18 month mouse study. Groups of 90 mice per sex per dose received 0, 5, 25, 500, 2500 or 5000 ppm (0, 0.66, 3.3, 66.6, 333.3, 666.6 mg/kg/d) in their diets. Clinical evaluations were made at 1, 2, 3, 6, 12 and 18 months. Ten animals per group were sacrificed at the 90 day time point for pathological evaluation. The 2500 ppm group was sacrificed at 12 months. Sporadic effects were observed on the body weight, food consumption, and organ weights. These were not dose related, resulting in a NOEL of 5000 ppm in diet for mice (111).

In the twenty-one day dermal rabbit study, the intact skin of male and female New Zealand White Rabbits received doses of 0, 125, 500 and 2000 mg/kg for 6 hrs/day for 21 days. Clinical signs observed were sporadic weight loss and diarrhea in a few rabbits. These effects were not dose related. Non dose related histological effects were observed in male rabbits. This effect was characterized as mild testicular atrophy occurring sporadically at all doses (112, 108).

Feeding studies in dogs have been done with purebred beagles. The animals received metsulfuron methyl in diets at dose levels of 0, 50, 500 and 5000 ppm (0, 0.2, 2, 20 mg/kg/d) for one year. There was a decrease in food consumption in the high dose males. There was a decrease in serum lactate dehydrogenase in all groups of both sexes at two or more doses these values were within the historical controls. The NOEL was 500 ppm in the males and 5000 ppm in females (112).

In a chronic feeding study in rats, the animals received metsulfuron methyl at doses of 0, 5, 25, 500, 2500 or 5000 ppm (0, 0.28, 1.4, 28.6, 143 or 286 mg/kg/d). Interim sacrifices were done at 13 and 52 weeks (105).

At the 13 week sacrifice there was a decrease in body weight in the 2500 and 5000 ppm groups; there was a decrease in absolute liver weight at 2500 and 5000 ppm males. There was a decrease in the relative liver weights in the 2500 and 5000 ppm females.

(a) In these discussions the assumptions made for estimated conversion of ppm (diet) to mg/kg/D were:

Species        Body weight (kg)  Intake (kg)
Rat 0.35 0.020 Mouse 0.03 0.004 Dog 10 0.4

When data were presented as ppm, the dose was estimated in mg/kg and is presented in parenthesis.

Findings at the 52 week sacrifice included increase in kidney weight (2500 ppm males) and increased absolute brain weights (at doses of 25, 500, 2500 and 5000 ppm) in males and at doses of 2500 and 5000 ppm in females. There was an increase in absolute heart weight at 2500 ppm in males and at 2500 and 5000 ppm in females. The absolute organ weights were back to normal at termination. Relative brain weights of the 2500 and 5000 ppm groups were increased (105)

**Oncogenicity Studies**
There were no gross or histopathological changes observed in mice receiving up to 5000 ppm metsulfuron methyl in their diets (112, 111). Similar results were obtained in the 104 week rat study; there were no histopathological changes observed which were attributable to metsulfuron methyl (105, 112). EPA concludes that there were no
oncogenic effects in rats or mice at the highest dose tested; 5000 ppm in both cases (9).

**Mutagenicity Testing**
Metsulfuron methyl was negative in the unscheduled DNA synthesis assay; in vivo bone marrow cytogenic assay in rats (doses were 500, 1000, and 5000 mg/kg bw); CHO/HGPRT Assay; *Salmonella typhimurium* reverse mutation assay four strains with and without S9 metabolic activation; and also in the in vivo mouse micronucleus assay at doses of 166, 500, 1666, 3000 and 5000 mg/kg (112). The only positive mutagenicity assay was in the in vitro assay for chromosome aberrations in Chinese Hamster Ovary at high doses (greater than 2.63 mM, 1.0 mg/mL)). In this assay no increases in structural aberrations were observed at 0.13 or 1.32 mM(0.05 or 0.5 mg/mL) (112).

**Developmental Studies**
Several studies have been done to investigate the effects of Metsulfuron methyl on reproduction and development in rats and rabbits.

Pregnant Cr1: COBS CD(SD) BR rats received metsulfuron methyl at doses of 0, 40, 250 or 1000 mg/kg by the oral route on days 5 to 14 of gestation. There were 25 rats per group. Maternal toxicity was observed at doses of 250 and 1000 mg/kg/d. The maternal toxicity NOEL was 40 mg/kg/d. There was no evidence of “teratogenic” response or embryo fetal toxicity (112).

In the rabbit study, New Zealand white rabbits received 0, 25, 100, 300 or 700 mg/kg/d on days 6 to 18 gestation. There was a dose related increase in maternal deaths; 1, 2 and 12 deaths at doses of 100, 300 and 700 mg/kg respectively. The maternal toxicity NOEL was 25 mg/kg/d and there was no evidence of teratogenic or embryolethal effects observed in this study (112).

Several multigenerational studies have been done with Metsulfuron methyl. A four litter reproduction study was done concurrently with the chronic bioassay. Rats from each treatment were separated from the main study and bred. The doses were 0, 5, 25, 500, 2500, and 5000 ppm (0, 0.28, 1.4, 28.6, 143 and 286 mg/kg/d). There was a dose dependent decrease in body weight in the parental (P1) generation at doses of 25 ppm and greater in males and females. This effect was not present in dams during gestation or lactation (106).

Overall fertility in the P1 and filial (Fl) matings was low in both control and treated groups with no apparent cause. There was a decrease in pup size in the Fla but not the Flb, F2a, or F2b litters. The gestation index was 100% for all groups in both filial generations with the exception of F2a when it was 90%. On the basis of the lower body weights and lower growth rates, the NOEL was 25 ppm for this study (106).

In a 90 day, 2 generation 4 litter protocol, rats received 0, 25, 500 or 5000 ppm (0, 1.4, 28.6, 286 mg/kg/d) Metsulfuron methyl in their diets for 90 days prior to mating. In this protocol the parental generation was bred twice first to produce the Fla and then the Flb. The Flb rats were then fed the appropriate diet for 90 days (after weaning). There was a decrease in litter size in the 500 ppm group in the F2a generation, but not in any other generation. The NOEL for this study was 500 ppm (107).

In a 90 day feeding, one generation rat study, 16 male and 16 female rats received 0, 100, 1000 or 7500 ppm in their diet prior to mating. There were no differences observed in reproduction and lactation performance or litter survival among groups. There was an overall low fertility in the control and treated groups. This result made the effects of metsulfuron methyl on fertility difficult to assess from this study (104).

**Tolerances and Guidelines**
Tolerances have been set for metsulfuron methyl in barley wheat (from 0.05 to 20 ppm, depending on the commodity) and in meat and meat byproducts (0.1 ppm). The tolerance in milk is 0.05 ppm (8, 9). The acceptable daily intake is 0.0125 mg/kg/d based on a one year dog NOEL of 1.25 mg/kg/d using a safety factor of 100 (9).

**Avian**
Metsulfuron methyl has been tested in two species of birds, the mallard duck and the bobwhite quail. The acute oral LD50 is greater than 2150 mg/kg in the duck. Two, 8 day dietary studies have been done. The 8 day LC50 is greater than 5620 ppm in both the duck and the quail (9).
Invertebrates

The 48 hour LC50 for Daphnia is greater than 150 ppm and the acute toxicity in the honeybee is greater than 25 mg/bee (9).

Aquatic

Metsulfuron methyl has acute LC50 of greater than 150 ppm in both the rainbow trout and the bluegill sunfish (9).

Summary

Metsulfuron methyl has a moderate to high mobility in the soil profile and is relatively persistent in the environment, especially when applied in the fall. These factors would be of concern under most circumstances. However, metsulfuron methyl is applied at very low rates (3-4 ozs./A) and therefore the amounts which reach the soil are quite low. Consequently, Metsulfuron methyl should not impact groundwater as a result of leaching or migrate from the target area. Metsulfuron methyl has low toxicity (EPA Toxicity Category III) for acute dermal exposure and primary eye irritation and is category IV for all other acute exposures. The chronic studies indicate no oncogenicity response and the systemic NOEL’s are 500 ppm in rats and 5000 ppm in mice. There was no evidence of teratological effects in the rat or the rabbit at the highest dose tested in both species. While there was evidence of maternal toxicity at 40 mg/kg/d in the rat and 100 mg/kg/d in the rabbits.

REFERENCES

2. Farm Chemicals Handbook: 1985

9. EPA Pesticide Fact Sheet Metsulfuron methyl: 1986 Collection of pesticide chemistry
   Pub. by US Government Printing Office 461-221/24041


103. DuPont Field Soil Dissipation of [Phenyl (U) - 14C] Metsulfuron Methyl on United States and Canadian Soils (AMR 476-86).

104. DuPont HL 180-82; 90 day feeding one generation Reproduction Study in Rats.

105. DuPont HLO-61-85; Chronic Feeding Study with Concurrent Two Generation Reproduction Study in Rats - Chronic.


107. DuPont HLR-524-84 Two generation, Four Litter Reproductive Study in Rats.

108. DuPont HLR 137-83 Subchronic Dermal Study (21 Days) in Rabbits.

111. DuPont HLR 463-84 Ninety-Day and Long Term Feeding Study in Mice.

112. Ally Herbicide Product Monograph
TRICLOPYR

In addition to the review that is presented below, a comprehensive review available from USDA Forest Service provides information that incorporates more recent studies and data. The US Forest Service risk assessment report is available at: http://www.fs.fed.us/foresthealth/pesticide/risk.shtml

Review conducted by MDAR and MassDEP for use in Sensitive Areas of Rights-of-Way in Massachusetts

Common Trade Name(s): Garlon 3A, Garlon 4
Chemical Name: Triclopyr [(3,5,6-Trichloro-2-pyridinyl) oxy] acetic acid
CAS No: 55335—06—3

GENERAL INFORMATION

Triclopyr is a picolinic acid derivative and is marketed as Garlon 3A the triethylamine (TEA) salt (CAS #057213-69-1) and Garlon 4 the butoxyethyl ester (CAS# 008008-20-6).

Triclopyr is effective against a wide variety of woody plants as a foliar spray, basal spray and when applied to cut surfaces. Triclopyr is absorbed by both plant leaves and roots and is readily translocated throughout the plant. It produces an auxin-type response in growing plants in that it appears to interfere with normal growth processes. Thus, maximal plant response occurs when applications are made soon after full leaf development and when there is sufficient soil moisture for plant growth.

ENVIRONMENTAL FATE

Mobility

Most laboratory and field studies indicate that Triclopyr is a relatively mobile herbicide under most conditions. Soil organic carbon partition coefficients K(oc) were determined for the TEA salt in 12 soils which ranged from 0.081% to 21.7% organic carbon. The K(oc) values range from 12 to 78 (14), indicating that Triclopyr should be mobile in most soils. In the same study the K(oc) values of trichloropyridinol, the major metabolite, were reported to range from 114 to 156 in three soils which were not identified. This indicates that trichloropyridinol is less mobile than Triclopyr and should have moderate mobility in soil(14).

In a laboratory study using sandy loam soil with a low organic matter content (0.62%), 75-80% of the applied Triclopyr leached through a 12 inch soil column between days 11 and 15. Water was applied at the rate of 0.5 inches/day for 45 days. The major degradation product, trichloropyridinol required 13 inches of applied water to elute, nearly twice as much (7.5 inches) as Triclopyr(14).
In a field study, Garlon 3A was applied at the rate of 3 gallons/acre (9 lbs/acre) to six soils ranging from clays to loamy sands in six states. Rainfall was reported to be normal, but not given. Small amounts of Triclopyr and its metabolites were found in the 6–12 inch and 12-18 inch layers of soil 28 to 56 days after application (14,15). Although an application rate of 9 lbs per acre is rather high, the presence of Triclopyr at those depths should be noted especially since there is a correlation with the previous laboratory studies.

In other studies, Triclopyr exhibited significantly lower mobility than had been previously reported. In a field study conducted in Massachusetts, Triclopyr was applied to sandy loam soil at a rate of 0.6 lb/acre. Rainfall was reported as normal, but not given. Triclopyr was never detected below the top ten inch layer of soil at any time during the three month study (100). As part of the same study, Triclopyr was applied to soil columns containing the same soil as in the field study at the rate of 0.6 and 6.0 lbs/acre. Simulated rainfall was applied to the soil columns at a rate of 1 inch per week for a total of 5 inches. Triclopyr was not detected below the top 4 inch layer of soil (100). These results indicate lower mobility than previously reported, but they may reflect the short persistence of Triclopyr in soil rather than its mobility through the soil profile.

Persistence

Soil

Microbial degradation is the primary mechanism by which Triclopyr is degraded in soils to two metabolites (15). Degradation under anaerobic conditions (i.e. saturated soils) is reported to be 5 to 8 times slower than under aerobic conditions (14). Triclopyr in soils is not thought to be degraded to any appreciable extent by chemical hydrolysis and, due to its low volatility, is not thought to volatilize from soil to any great extent (15).

A review by TRW states that Triclopyr “is not considered to be a persistent compound in soils” (95). Studies indicate that under certain conditions the half-life of Triclopyr can be relatively short. The Dow Chemical Company has reported a half-life of 10 days in silty clay loam (96). In a small West Virginia watershed the half-life was estimated as between 14 and 16 days (15). Triclopyr was applied aerially at the rate of 10 lbs/acre, but much of the Triclopyr was intercepted by foliage. Average Triclopyr residues in soil from the treated area of this study, measured on the day of the treatment, were non—detectable in densely wooded areas, 4.4 ppm in lightly wooded areas, and 18 ppm in open areas (15). In a Massachusetts field study, the half—life of Triclopyr was reported as 10 days after the applications of 0.6 and 6.0 lbs/acre Triclopyr to non-target vegetation (100).

Most other studies suggest a much longer persistence for Triclopyr in soil. In a laboratory study, Dow reported a half-life of 46 days for Triclopyr in loam. The loam was maintained in the laboratory at 95 deg F with moisture at field capacity for the duration of the study (96). A 95 deg soil temperature and moisture at field capacity are both quite high and indicate that the persistence at less than ideal conditions would be longer. Dow also reports the average half-life of Triclopyr in soil to be 30 days (101). An average half-life of 46 days is reported in the Herbicide Handbook (10) and by Ghassemi et al. (95). In addition, other investigators have reported a half—life in soil of “less than 50 days” at temperatures between 25-35 deg C, and between 79 and 156 days at 15deg C (14). In a field study conducted in Sweden, Garlon 3A was applied at the rate of 2 lbs (a.i.)/acre to eight different forest soils. Residues of Triclopyr persisted for 1 to 2 years, and in some cases in excess of 2 years, at levels approximately 10 percent or less of initial soil residue levels (15). It must be noted that soil temperature levels never exceeded 14deg C (57 deg F) and these temperatures are not favorable to microbial degradation (15). These low maximum temperatures are not typical of year round Massachusetts temperatures, but indicate the increased persistence that may occur when applications are made in the fall and are followed by cold weather.

The variable half-lives reported for Triclopyr indicate that soil half-life may be dependent on the soil and climatic conditions. As in most situations of microbial degradation; cold and, dry or saturated soils decrease the decomposition rate, while warm moist soils increase it.
Aquatic

The fate of the butoxyethyl ester of Triclopyr (TBEE) in water is summarized in Figure 1. This diagram shows the major degradation pathways for the ester in water, but does not include processes such as sediment and particulate adsorption. The fate of the ester in water has also been simulated with a modelling technique by McCall et al., 1988 (115). A recent study by Woodburn (116) with the triethylamine salt of Triclopyr experimentally applied to a lake in Florida also provides useful comparative data on the persistence of Triclopyr degradation products. The degradation path is believed to be TBEE to Triclopyr acid to 3,5,6—trichloro-2-pyridinol (TCP) to non-halogenated organic acids.

TBEE degrades quite rapidly in water to Triclopyr acid. Laboratory studies indicate that photolysis is the principal degradation pathway with hydrolysis also contributing (117, 118). Several studies indicate that the half-life of the ester in water can range from 1.5—2 days as a result of photolysis (117, 119). Hydrolysis half—lives are dependent upon water pH and temperature and range from 0.06 d to 208 d in natural waters. They decrease with increasing temperature and increasing pH. Acidic conditions increase the persistence of the ester substantially. The 208 d half—life was observed in natural unbuffered water at pH 5 and 15 °C. Waters with this pH level occur in Massachusetts. One laboratory study has produced contradictory results where the ester was stable to hydrolysis, and little photodegradation of the ester occurred over 9 months (120). This study however was performed with buffered, sterile water. Modelling results for the dissipation of the ester indicate that decay should be fairly rapid with a half-life of 12-18 hours (115).

The acid is short-lived in the aquatic environment with reported half—lives of from 2.1 hours at the water’s surface in summer at 40deg N latitude to 14 hr at 1m water depth in winter (117). The principal decay product of the acid is 3,5,6-trichloro-2-pyridinol (TCP), a transient metabolite in water with half—lives ranging from minutes to one day (121). TCP rapidly degrades into nonhalogenated, low molecular weight organic acids (116,121), with phototransformation playing a larger role than hydrolysis in this process.

Salomon et al. (118) demonstrated a half—life of 3.8-4.3 days at l6-17 deg C for the ester to TCP step in an Ontario Lake. Woodburn (116) added Triclopyr salt to a Florida lake and determined a half—life of 0.5—3.6 d at 300 C for the salt to organic acid step. The time scales of both of these studies are in general agreement with the other data on the time course of breakdown for the ester (or salt) to organic acids. With the exceptions of the Hamaker (120) study and a slow breakdown at pH 5, most studies indicate that TBEE in water is degraded relatively rapidly.

TOXICITY REVIEW

Acute (Mammalian)

The Triclopyr toxicity database has been reviewed in several places including the GEIR on the Control of Vegetation on Utility and Railroad Rights-of-Way in Massachusetts (14), Herbicide Handbook Weed Science Society of America (10), and by the U.S. Forest Service (15). Several Dow Publications review the Triclopyr information (101) and Garlon products (102 and 103).

The oral LD5O for Triclopyr in rats is 729 mg/kg in males and 630 mg/kg in females (15, 101). The rat oral LD5O for combined sexes has been reported as 713 mg/kg (10, 14). Rabbits and guinea pigs are more susceptible to oral administration of Triclopyr with LDSOs of 550 and 310 mg/kg respectively (14, 15, 10). The Garlon products have oral LD5Os of greater than 2000 mg/kg (10, 14, 15, 101, 103, 103).

The dermal LD5Os are greater than 2000 mg/kg in rabbits (Triclopyr), and greater than 3980 mg/kg in rabbits for Garlon 4 and Garlon 3A (101, 102, 103)
The effects of Triclopyr on the eye are dependent on the chemical derivative involved: the butoxyethyl ester found in Garlon 4 is essentially non—irritating (102, 15, 14, and 101), while the triethylamine salt is not only an irritant but can cause serious injury (101, 14, 15). These eye injuries include conjunctival irritation, moderate internal redness and moderate to severe corneal damage which may be permanent (14). An inhalation study showed that 100% of the test rats survived a 1 hour exposure to 3 to 20 dilutions of Garlon 3A in air. Transitory nasal irritation to rats was noted after a 4 hour exposure to Garlon 4 aerosol (14).

**Metabolism**

Two studies, one dermal and one oral have been done in humans to determine pharmacokinetic and metabolic profiles. Five mg/kg acid equivalent (ae) was applied to the forearm of 5 volunteers in the dermal study. One point five eight percent to 1.11% of the applied dose was absorbed and the percutaneous absorption half—life was 16.8 hours (108). In the oral study, 6 volunteers received 0.1 or 0.5 mg/kg Triclopyr (acid equivalent) in apple juice. The excretion half—life is 5 hours and 80% of the dose is recovered as unchanged Triclopyr in the urine (109). The 20% which was unaccounted for could be attributed to one of several explanations including incomplete collections of urine, incomplete absorption of material or metabolism to an unknown metabolite.

**Subchronic/Chronic Studies (Mammalian)**

Long—term bioassays have been done using Triclopyr in rats (107) and mice (106). Summaries of these studies, provided by Dow Chemical Company have been reviewed for this discussion.

Fischer 344 rats received 5, 20, 50 or 250 mg/kg/d in a preliminary 13 week study. There was a decrease in body weight gain at 50 and 250 mg/kg/d and kidney effects were observed in both sexes at doses of 20 mg/kg or greater (107). In the full two year study, the doses were 0, 3, 12 and 36 mg/kg/d. The dose related effects in the males were increased body weight at 12 and 36 mg/kg/d, and in females there was an increase in pigmentation in the proximal tubules at 3, 12 and 36 mg/kg/d. Neither the weight increase in the males nor the increased pigmentation in the females were accompanied by morphological, histological or functional changes. The NOAEL for males and females was reported to be 3 mg/kg/d (107).

In the mouse bioassay, ICR mice received Triclopyr in their diets for twenty-two months. The doses were 0, 50, 250, 1250 ppm (0, 5, 55, 28.6 and 143 mg/kg/d in males and 0, 5.09, 26.5 and 135 mg/kg/d in females). The range finding study included doses of 0, 200, 400, 800, 1600 or 3200 ppm. At the high dose there were decreases in body weight, anemia, changes in urine, increase in cholesterol levels and multiple changes in liver functions. Some of the liver changes were also observed in the 1600 and 800 ppm groups. There were decreases in body weights, changes in kidney and urine (at various doses and points in time) and liver effects at the 1250 ppm dose. At 250 ppm there were mild kidney effects and the NOEL was reported as 50 ppm (5.55 and 5.09 mg/kg/d for males and females respectively) (106).

In subchronic studies, the 90 day dietary NOELs were 30 mg/kg/d and 20 mg/kg/d for rats and mice, respectively. Dogs were more sensitive to dietary administration of Triclopyr, with kidney effects (decrease in excretion) at 2.5 mg/kg/d (14, 101). Dogs refused to eat food that would result in doses of 30 and 100 mg/kg (104). In a one year study, dogs received doses of 0. 0.5, 2.5 or 5.0 mg/kg/d. Minimal kidney effects were observed at 2.5 and 5.0 mg/kg/d. These findings were considered non—adverse by Dow making the NOAEL 5.0 mg/kg/d and the NOEL 0.5 mg/kg/d (105).

Two monkey studies were done to investigate kidney effects in primates. In one study, the monkeys received 0, 10, 20 or 30 mg/kg/d in diet for 28 days. There was no effect on urinary excretion or other responses observed (101, 104). In a second study, 4 monkeys received Triclopyr at 5 mg/kg/d for 28 days, the dose was then increased to 20 mg/kg/d for 102 days. The effects observed in this study were stool softening and diarrhea (104).
Oncocrenicity Studies
There have been two chronic bioassays done for Triclopyr. Rats received 0, 3, 12 or 36 mg/kg/d and mice received 0, 50, 250 or 1250 ppm (0, 5.55, 28.6, 143 mg/kg/d for males and 0, 5.09, 26.5 and 135 mg/kg/d for females). The only positive result was an increase in combined incidence of mammary adenomas and adenocarcinomas in the female rats at the high dose. There was no evidence of multiple tumors and the effect was not dose related (107, 106).

Mutagenicity Testing
Triclopyr has been tested for mutagenicity in a variety of test systems and found to be weakly positive in one, the dominant lethal study in rats. Triclopyr was non-mutagenic in bacterial assay systems, cytogenic assays, and mouse dominant lethal studies (15).

Developmental Studies
The teratology of Triclopyr was investigated using the rabbit model. Doses in the range finding study were 0, 25, 50, 100 and 200 mg/kg. There was 50% and 71% mortality in the 100 and 200 mg/kg groups respectively. The doses used in the full study were 0, 10, 25 and 75 mg/kg/d for days 6 to 18 of gestation. There were 16 rabbits per dose group. One dam in the 25 mg/kg/d group aborted and one dam in the 75 mg/kg/d group died. In the 25 mg/kg group one fetus had hyperplasia of the aortic arch with pulmonary arterial semilunar valve stenosis. Another fetus had a missing gall bladder. There was a statistically significant but non-dose related increase in resorptions at 10 mg/kg/d. This increase was within historical control variability. The developmental NOEL was reported as 75 mg/kg/d with a slight increase in maternal mortality (110)

Tolerances and Other Guidelines
Tolerances are set for Triclopyr on 5 raw agricultural commodities: grasses, forage (500 ppm); grasses, forage, hay (500 ppm); milk (0.01 ppm); meat, fat and meat by products (except liver and kidney) of cattle, goats, hogs, horses, and sheep (0.05 ppm); and liver and kidney of cattle, goats, hogs, horses, and sheep (0.5) ppm (8).

The Dow internal guideline for inhalation exposure to Triclopyr is 10 milligrams/cubic meter (102, 103).

Avian
The toxic effects of Triclopyr on birds have been investigated in a small number of studies conducted by the Dow Chemical Company. For mallard ducks, acute oral LC50s are reported at 1,698 mg/kg for unformulated Triclopyr, 3,176 mg/kg for Garlon 3A, and 4,640 mg/kg for Garlon 4. Eight day subchronic oral LC50s are reported as follows for the various triclopyr formulations:

Triclopyr
- mallard duck LC50 = 5,000 ppm
- bobwhite quail LC50 = 2,935 ppm
- Japanese quail LC50 = 3,278 ppm

Garlon 3A
- mallard duck LC50 = 10,000 ppm
- bobwhite quail LC50 = 11,622 ppm

Garlon 4
- mallard duck LC50 = 10,000 ppm
- bobwhite quail LC50 = 9,026 ppm

Source: (15)
The data summarized above indicate low acute and subchronic toxicity to the bird species tested. No field studies on the toxic effects of Triclopyr or its formulations in birds have been reported (15).

**Invertebrates**

Very little data were available on the invertebrate and microorganism toxicity of Triclopyr. The data reported are primarily for the triethylamine salt (Garlon 3A) and were generated by the Dow Chemical Company.

The data indicate low acute lethal toxicity* to organisms tested, with a 96 hr LC50 of 895 ppm in shrimp, 96 hr LC50 greater than 1000 ppm in crabs, and 48 hr LC50s ranging between 56 and 87 ppm in oysters (15). The 48 hr LC5O for Daphnia is reported as 1,170 ppm (15). After 72 hours of incubation with 500 ppm of Triclopyr, no apparent effects on growth were observed in six soil microorganisms when compared to a control (15).

No information was obtained on the invertebrate toxicity of Garlon 4, the butoxyethyl ester of Triclopyr.

**Aquatic**

The available information on Triclopyr toxicity to fish indicate a wide response of fish to the two formulations of Triclopyr and to unformulated Triclopyr. The butoxyethyl ester of Triclopyr (Garlon 4) is "highly toxic to fish", based upon the Clarke et al. criteria. The 96 hour LC5O values for rainbow trout and bluegill sunfish are 0.74 and 0.87 ppm respectively (15). The corresponding value for juvenile Coho salmon is 1.3 ppm (122).

The triethylamine salt formulation (Garlon 3A) is "slightly toxic" to fish with 96 hour LC5Os of 552 and 891 ppm for rainbow trout and bluegills respectively. The corresponding values for unformulated Triclopyr are 117 ppm for rainbow trout and 148 ppm for bluegill. Both fish species were less sensitive to Garlon 3A than to the active ingredient (15).

No fish toxicity data are available for 3,5,6—trichloro—2—pyridinol (TCP), the intermediate breakdown product from the Triclopyr acid to the non—halogenated organic acid end product.

Dow Chemical Company reports that in natural soil and aquatic environments, both amine and ester formulations rapidly convert (photodegrade) to Triclopyr acid, which in turn is neutralized to a salt at normal environment pH (5.5-6.5)(15). No information is provided with any of the fish toxicity data on the actual form of Triclopyr present in the test water. The persistence data summarized in a previous section and the simulation results of McCall et al. (115), however provide a description of the probable fate of Triclopyr in the toxicity test tanks. The majority of the fish mortalities during the toxicity tests with bluegill sunfish and rainbow trout exposed to the ester occurred during the first 24 hours of the test: a pattern consistent with the change of the toxic ester form to less toxic breakdown products during this period (124).

**EXPOSURE ASSESSMENT**

For the exposure assessment, we have chosen to analyze the fate of the butoxyethyl ester form of Triclopyr (Garlon 4) in water because of its reported high aquatic toxicity in laboratory studies. Garlon 4 would be applied basally at an average application rate of 0.5 pints per acre for the proposed utility program.

In aquatic organisms, LC5Os greater than 10 ppm are considered to be indicative of only slight toxicity and LC5Os less than 1 ppm are considered to reflect high acute toxicity (Clarke et al., 1970 as referenced in [15]).
Since Garlon 4 contains 61.6% of the active ingredient, this application could distribute 37 mg Triclopyr BEE/m². The requested maximum application rate is 2 pints per acre.

Two aquatic exposure scenarios have been constructed to evaluate the potential contamination of non-target surface waters with Garlon 4 from a typical land application. The first, most extreme, and very unlikely scenario is for the case of a static stream traversing a treated acre with a percentage of all of the herbicide applied to the acre running into the water. The second represents a more shallow, static stream or standing water body of much less volume with runoff from a portion of the bordering land.

**SCENARIO (1)**

**ASSUMPTIONS:**
- Application rate = 0.5 pint/acre
- 0.47 L/pint
- 61.6% active ingredient
- 20% of herbicide applied to acre runs off
- density of applied herbicide = 1.0 g/ml

**RUNOFF:**

\[0.20 \times 0.5 \text{ pt/acre} \times 0.47 \text{ L/pt} \times 0.616 = 0.03 \text{ L/acre}\]

**RECEIVING WATER:**

Static stream crossing a treated acre
- Dimension: 0.3 x 1.22 x 64 m = 23.4 m³ (volume)

**DILUTION:**

\[0.03 \text{ L into } 23.4 \text{ m}^3 = 1.3 \text{ mL/m}^3\]
\[1.3 \text{ mL/m}^3 \times 1 \text{ m}^3 /10^{-3} \text{ L} = 1.3 \times 10 \text{ mL/L}\]
\[1.3 \times 10^{-3} \text{ mL/L} \times 1 \text{ g/ml} \times 10^3 \text{ mg/g} = 1.3 \text{ mg TBEE/L}\]

**SCENARIO (2)**

**ASSUMPTIONS:**
- Application Rate = 0.5 pt/acre
- 0.47 L/pt
- 61.6% active ingredient
- 20% of herbicide applied to 3 m² runs off
- density of applied herbicide = 1.0 g/ml

**RUNOFF:**

\[0.2 \times 0.5 \text{ pt/acre} \times 0.47 \text{ L/pt} \times 0.616 \times 2.47 \times 10^{-4} \text{ acre/m}^2 \times 10 \text{ mL/L} \times 3 \text{ m}^2 = 0.02 \text{ mL}\]

**RECEIVING WATER:**

Static stream,
- Dimensions: 0.15 x 1 x 5 m = 0.75 m³ (volume)

**DILUTION:**

\[0.02 \text{ mL into } 0.75 \text{ m}^3 = 0.03 \text{ mL/m}^3\]
\[0.03 \text{ mL/m}^3 \times 10^{-3} \text{ m}^3 /10 \text{ mL/L} \times 10^{-3} \text{ mg/g} \times 1 \text{ g/ml} = 0.03 \text{ mg/L}\]

The calculations presented above illustrate that the probable immediate post—runoff concentrations of TBEE in static water bodies will be in the sub-parts per million range. At maximum application rates (2 pts/acre), these concentrations would range from about 0.1 to 5.2 mg/L. The concentrations for the worst exposure scenario (#1) are greater than (7x) the 96 hour LC50 concentrations for freshwater fish; those
for the other scenario are almost an order of magnitude less. The no effect level for TBEE with juvenile Coho salmon is \( \leq 1.0 \text{ mg/L} \) (122). Therefore, under the worst exposure scenario with the maximum application rate of herbicide, the 96 hour LC50 could be exceeded. Under other, less extreme conditions at average application rates, predicted concentrations of the active ingredient would be substantially less than the reported no effect level in Coho salmon. The persistence characteristics of TBEE are such that the ester form of Triclopyr would not likely persist in surface waters for longer than a couple of days, except in those waters in Massachusetts which are acidic where the ester may persist for up to several months. It is also very unlikely that rainbow trout would be impacted at application rates of 0.5 pts/acre based on the reasonable scenario (#2) which predicts water concentrations of Garlon 4 less than toxic concentrations.

The following factors would also tend to reduce the exposure concentrations that fish would experience: flowing waters would provide greater dilution than assumed for static conditions; the Massachusetts Right-of-Way Management Act mandates an application setback of 10 feet from standing or flowing waters or from wetlands (33 CMR 11.04:(1) and (4) (a)); and actual runoff of the applied herbicide would probably be less than used for these sample calculations. Scenario 1 represents an extremely unlikely event where 20% of all the herbicide applied to an acre runs off into a small water course. The conditions which would foster this type of runoff across setbacks (i.e. heavy rains) would tend to turn static stream systems into flowing water courses and hence increase dilution.

The application rate used in the previous non—target species assessment (June 23, 1990) was 0.5 pints per acre applied basally. The utilities involved in managing rights-of-way and the manufacturer of Garlon 4 have since indicated that the required application rate may range as high as 2-3 quarts of Garlon 4 per acre for effective control of vegetation. The following addition to the exposure assessment examines the resultant changes in the predicted exposure concentrations that might occur in freshwater fish habitats when Garlon 4 is applied at the 2-3 quarts /acre.

The change in the application rate will result in the following differences in predicted exposure concentrations from those originally predicted for 0.5 pts/acre:

\[
\begin{align*}
2 \text{ at/acre} \times 2 \text{ pt/qt} & = 8 \times 0.5 \text{ pt/acre} \\
3 \text{ at/acre} \times 2 \text{ pt/qt} & = 12 \times 0.5 \text{ pt/acre}
\end{align*}
\]

Application rates will therefore be 8-12 times greater than for the 0.5 pts/acre case. The probable concentrations in water after runoff as previously predicted were 1.3 (Scenario 1) and 0.03 mg/L (Scenario 2) ing butoxyethyl ester of Triclopyr / L. These concentrations would therefore range from 0.24 — 15.6 ing/L for application rates between two and six quarts.

These predicted concentrations encompass and substantially exceed the reported LCSO concentrations for fish (in range of 0.7 - 1.3 mg/L and the NOEL of 1 mg/L for juvenile Coho salmon. The more realistic exposure scenario (#2) predicts exposure concentrations of the same order of magnitude as the LC50 values.

Given that the higher application rates required for vegetation control in some areas have the potential to produce potentially lethal concentrations of the butoxyethyl ester of Triclopyr to fish in water as a result of runoff, a setback greater than the mandated 10 feet from standing or flowing waters (333 CMR 11.04: (1) and (4) (a) ) will provide an additional level of protection when application rates exceed 0.5 pts/acre.

**SUMMARY**

Triclopyr exhibits moderate mobility in most of the soils tested. Soils with higher organic carbon content would be expected to retard the mobility of Triclopyr. Trichloropyridinol, the major breakdown product, is less mobile than Triclopyr.
Microbial degradation is the primary mechanism by which Triclopyr is degraded in soils. Degradation rates are variable and appear to be dependent on the soil and climatic conditions. In Massachusetts conditions, Triclopyr can be expected to have moderate persistence when applied in warm weather (late spring—early fall), and slightly longer persistence in colder weather. 713 mg/kg. Rabbits and guinea pigs have oral LDSOs of 550 and 310 mg/kg respectively. The target organ for Triclopyr is in the liver. The only positive result in the oncogenicity studies was an increase in the combined incidence of mammary adenomas and adenocarcinomas in the female rats at the high dose. Mutagenicity tests were negative. The developmental NOEL was reported as 75 mg/kg/d with a slight increase in maternal mortality. Using EPA’s carcinogen classification scheme, Triclopyr may be considered a group C carcinogen (possible human carcinogen: limited animal evidence).

RECOMMENDATION

The herbicide Garlon 4, containing the butoxyethyl ester of Triclopyr (EPA Reg. No. 464-554), is recommended for use in sensitive areas only at application rates of 0.5 pt/acre pursuant to 333 CMR 11.00. Applications at rates up to three quarts per acre are permitted with a setback of 50 feet from standing or flowing waters suitable for fish habitat. The set back restriction may be waived upon demonstration to both the Departments of Food and Agriculture and Environmental Protection that runoff concentrations from applications of Garlon 4 with setbacks less than 50 feet do not pose a threat to fish.

REFERENCES


101. Dow Environmental and Toxicology Profile of Garlon Herbicides. Technical Data Sheet.


103. Dow MSDS Sheet for Garlon 3A.

104. Personal communication with Dr. David Eisenbrandt 12/30/88.


115. Dow Chemical USA. Letter from Dr. Frank A. Kidd to Mr. Lee Corte Real, MA DFA. Dated 9/21/89.


120. McCarty, W.M., and H.C. Alexander. n.d. Toxicity of Triclopyr, ethylene glycol butyl ether ester to freshwater organisms. Unpublished report. Environmental Sciences Research Laboratory, Dow Chemical USA