# <u>EXTOXNET</u>

#### **Extension Toxicology Network**

A Pesticide Information Project of Cooperative Extension Offices of Cornell University, Michigan State University, Oregon State University, and University of California at Davis. Major support and funding was provided by the USDA/Extension Service/National Agricultural Pesticide Impact Assessment Program.

Pesticide

Information

# Metribuzin

Profile

Publication Date: 9/93

### **TRADE OR OTHER NAMES**

Some trade names include Bay 94337, Bay DIC 1468, Lexone, Sencor, Sencoral and Sencorex (<u>17</u>).

## **REGULATORY STATUS**

The United States Environmental Protection Agency (EPA) issued a registration standard in 1985 which gave metribuzin a restricted use classification because of questions regarding groundwater contamination and chronic toxicity. However, these questions were later resolved when manufacturers submitted necessary information. The restricted use status was removed and it is now classified as a general use pesticide (10, 12). Products containing metribuzin must bear the signal word "Caution" (17).

## INTRODUCTION

Metribuzin is a selective triazinone herbicide which inhibits photosynthesis. It is used for control of annual grasses and numerous broadleaf weeds in field and vegetable crops, in turfgrass, and on fallow lands. Metribuzin is available as liquid suspension, water dispersible granular, and dry flowable formulations (2, 17).

## **TOXICOLOGICAL EFFECTS**

# ACUTE TOXICITY

Metribuzin is slightly to moderately toxic to humans by oral, skin or inhalation routes of exposure (<u>18</u>). Sedation and labored breathing were observed in metribuzin poisoned rats. Deaths occurred within 24 hours, while survivors recovered slowly

without permanent effects (5). No effects were observed in rats exposed to an aerosol concentration of 31 mg/m3 for 6 hours/day, five days/week, for 3 weeks.

No effects were observed in rats given dermal doses of 1,000 mg/kg/ day for 3 weeks (20). Metribuzin was not irritating to the skin or eyes of rabbits or of human volunteers. Dermal application did not cause skin sensitization (5, 16). Acute inhalation exposure may cause irritation of the mucous membranes of the upper respiratory tract (9).

The amount of metribuzin that is lethal to one-half (50%) of experimental animals fed the material is referred to as its acute oral lethal dose fifty, or LD50. The oral LD50 for technical metribuzin in rats is 1,090 to 2,300 mg/kg; in mice it is 700 mg/kg, and in guinea pigs is 245 to 274 mg/kg. The dermal LD50 in rabbits is greater than 20,000 mg/kg. The lethal concentration fifty, or LC50, is that concentration of a chemical in air or water that kills half of the experimental animals exposed to it for a set time period. The 4-hour LC50 for metribuzin in rats is greater than 885 mg/m3 (5, 12, 17, 18, 20).

## **CHRONIC TOXICITY**

Two-year feeding studies with rats and dogs resulted in no observable effect levels (NOEL) of 5 mg/kg for rats and 2.5 mg/kg for dogs (1, 18). Reduced weight gain, an increase in the number of deaths, blood chemistry changes, and liver and kidney damage were observed in a two-year study in which dogs were given 1,500 ppm or 37.5 mg/kg of metribuzin (12, 20). No ill effects were observed in dogs fed dietary doses of 12.5 mg/kg for three months (5). In a 3-month study with rats given dietary doses of 0, 2.5, 7.5, 25 or 75 mg/kg of metribuzin, no effects were apparent in rats receiving 2.5 mg/kg. At doses of 25 and 75 mg/kg, enlarged livers and thyroid glands were observed (<u>18</u>).

EPA has established a Lifetime Health Advisory (LHA) level of 200 ug/l (ppb) for metribuzin. Water containing metribuzin at or below this level is acceptable for drinking every day over the course of one's lifetime, and does not pose any health risk. However, consuming very high levels of metribuzin over a long period of time has caused kidney damage in test animals (<u>18</u>).

#### **Reproductive Effects**

Doses of 15, 45 or 135 mg/kg/day of technical metribuzin were administered by gavage to rabbits on days 6 through 18 of pregnancy. Body weight gain decreased at 135 mg/kg. No effects on the mothers were observed from doses at or below 45 mg/kg. No effects on the fetuses were observed at any of the doses tested (<u>18</u>). A

three-generation study in rats, at 35, 100, and 300 ppm, showed no influence on reproduction (1, 16).

#### **Teratogenic Effects**

No evidence of teratogenic effects were observed in rabbits given 135 mg/kg/day, the highest dose tested. Metribuzin did not have embryotoxic or teratogenic effects in tests on rats (highest dose tested: 100 mg/kg/day) (1).

#### **Mutagenic Effects**

Tests on live animals and on tissue cultures have shown no mutagenic activity  $(\underline{16})$ .

#### **Carcinogenic Effects**

There were no indications of carcinogenic effects in rats fed 35, 100, and 300 ppm for two years, nor in mice fed 20, 800 and 3,200 ppm for two years (1, 16). EPA has stated that data from these and other laboratory studies are inadequate to determine if metribuzin causes cancer. Metribuzin remains unclassified by the EPA regarding its carcinogenicity (18).

#### **Organ Toxicity**

In single high doses, metribuzin appears to depress the central nervous system. It affects the thyroid gland and stimulates metabolic enzymes of the liver if given in repeated doses (1). No organ changes were seen in fatally poisoned rats that died within 24 hours, nor in survivors of excess metribuzin doses ( $\underline{5}$ ).

#### Fate in Humans and Animals

The breakdown of metribuzin in animals is not fully understood (<u>12</u>). Reportedly, after metribuzin is absorbed, it is rapidly distributed in the body and excreted unchanged in the urine (<u>1</u>). In warm-blooded animals, 90% elimination occurs within 96 hours, about equally distributed between the urine and feces (<u>6</u>).

### **ECOLOGICAL EFFECTS**

#### **Effects on Birds**

Data indicate that metribuzin is moderately toxic to birds on an acute oral basis, and that it is slightly to non-toxic to upland birds when it is given in the diet ( $\underline{12}$ ). The LD50 values are greater than 100 mg/kg for bobwhite quail, mallard ducks, canaries,

red-winged blackbirds, brown headed cowbirds, common grackles, and house sparrows (<u>14</u>, <u>18</u>). The LD50 in Japanese quail is 168 mg/kg, in mallard ducks is greater than 460 mg/kg, and in bobwhite quail is greater than 164 mg/kg (<u>16</u>, <u>17</u>).

#### **Effects on Aquatic Organisms**

Metribuzin is slightly toxic to fish. The 96-hour LC50 in rainbow trout is 64 to 76 mg/l, 80 mg/l in bluegill sunfish, and is greater than 10 mg/l in goldfish (6, 12, 15, 17).

#### Effects on Other Animals (Nontarget species)

Metribuzin is moderately toxic to freshwater invertebrates; the 96-hour LC50 for marine/estuarine shrimp is  $48.3 \text{ mg/l} (\underline{12})$ . It is non-toxic to bees (<u>6</u>, <u>8</u>, <u>17</u>).

Endangered plant species, especially those growing on or near treated rights-of-ways, may be jeopardized by exposure to metribuzin. Before applying metribuzin to specific areas in which endangered species are known to be found, applicators are required to determine that no such species are located in or adjacent to the area to be treated. Information can be obtained from the Endangered Species Specialist at a regional office of the U.S. Fish and Wildlife Service (12).

### **ENVIRONMENTAL FATE**

#### Breakdown of Chemical in Soil and Groundwater

Metribuzin is highly soluble in water and has a low tendency to adsorb to most soils (18). It has a moderate ability to adsorb to soils with high clay and/or organic matter content. In sandy soils that are low in clay and organic matter, the herbicide is readily leached (12, 21). The EPA considers metribuzin to be one of a group of pesticide compounds that has the greatest potential for leaching into, and contaminating, groundwater (11). It has been detected in Ohio rivers and Iowa wells and groundwater (13, 18). It should not be applied where the water table is close to the surface or where soils are very permeable, such as on well-drained soils or loamy sands (12).

The major mechanism by which metribuzin is lost from soil is microbial degradation. Any condition which favors activity of soil microorganisms will increase the rate of breakdown. Losses due to volatilization or photodegradation are not significant under field conditions (21).

The persistence of metribuzin is determined by its rate of adsorption to soil particles, which is closely related to the organic matter content of the soil. In soils with a high

organic matter content, adsorption is increased, loss through leaching is prevented, and the half-life can be stretched to several months. Other soil characteristics, such as low soil moisture, low temperatures, and acidic conditions, may also increase the persistence and adsorption of the class of herbicides in which metribuzin is included, the triazines. Metribuzin residues have carried over into the season following treatment, especially on muck soils (7). The half-life of metribuzin varies according to soil type and climatic conditions. Soil half-lives of less than one month to 6 months have been reported (<u>18</u>).

#### **Breakdown of Chemical in Water**

The half-life of metribuzin in pond water is approximately seven days ( $\underline{6}$ ). The hydrolysis half-life of metribuzin is nine to 28 weeks ( $\underline{13}$ ).

#### **Breakdown of Chemical in Vegetation**

Metribuzin is absorbed through the leaves when plants are given surface treatment, but the primary route for uptake is through the root system. From the roots, it is translocated upward, becoming concentrated in the roots, stems, and leaves of treated plants (<u>12</u>).

## PHYSICAL PROPERTIES AND GUIDELINES

Metribuzin is a white, crystalline solid with a slightly sharp, sulfurous odor. It is stable in acidic and alkaline solutions. The pure compound is colorless, with a mild, chemical odor. Technical metribuzin is white to yellowish with a slightly sharp, sulfurous odor. Metribuzin is nonflammable and noncorrosive and stable under normal temperatures and pressures. It may burn if exposed to heat or flame, but it does not readily ignite Thermal decomposition may release toxic fumes of oxides of carbon, nitrogen and sulfur (1, 4, 14, 15, 16, 20, 21).

#### **Occupational Exposure Limits:**

ACGIH TWA:	5 mg/m3
OSHA TWA:	5 mg/m3
NIOSH recommended TWA:	5 mg/m3 ( <u>20</u> )

#### **Physical Properties:**

CAS #: 21087-64-9 Specific gravity: 1.28 Solubility in water:

1,200 ppm at 20 degrees C (<u>18</u>)

Solubility in other solvents: soluble in aromatic and chlorinated hydrocarbon solvents  $(\underline{12})$ .

	Solvent	g/100 g solvent at 20 degrees C
	Dimethyl formamide	17
	cyclohexane	100
	acetone	82
	methanol	45
	benzene	22
	ethanol	13
	xylene	9
	kerosene	< 1 ( <u>14</u> )
Melting point:	125 to 126.5 degrees C (261 degrees F) ( <u>1</u> , <u>12</u> )	
Vapor pressure:	less than 10 to the minus 5 mm Hg at 20 degrees C ( $16$ , $18$ )	
Koc:	41 g/ml ( <u>18</u> )	
Kd:	0.11, 0.37 ( <u>13</u> )	
Chemical Class/Use:	Triazole herbicide	

### **BASIC MANUFACTURERS**

Mobay Corporation P.O. Box 4913 Kansas City, MO 64120

#### **Review by Basic Manufacturer - Mobay:**

Comments solicited: October, 1992 Comments received: November, 1992

Du Pont Agricultural Products Walker's Mill, Barley Mill Plaza PO Box 80038 Wilmington, DE 19880-0038

#### **Review by Basic Manufacturer - Du Pont Agr.:**

Comments solicited: October, 1992 Comments received: November, 1992

### REFERENCES

- 1. American Conference of Governmental Industrial Hygienists, Inc. 1986. Documentation of the threshold limit values and biological exposure indices. Fifth edition. Cincinnati, OH: Publications Office, ACGIH.
- 2. Berg, G.L. (ed.). 1986. Farm Chemicals Handbook. Willoughby, Ohio: Meister Publishing Co.
- Cohen, S. Z., et al. 1986. Monitoring groundwater for pesticides. Office of Pesticide Programs (TS-769C), U. S. Environmental Protection Agency. Published by the American Chemicals Society. Washington, DC.
- 4. DuPont de Nemours and Company. 1983. Technical data sheet for metribuzin. Agricultural Chemicals Department. Wilmington, DE: DuPont.
- 5. Gosselin, R.D., et al. 1984. Clinical toxicology of commercial products. Fifth edition. Baltimore. Williams and Wilkins.
- 6. Hartley, D. and H. Kidd, eds. 1983. The agrochemicals handbook. Nottingham, England: Royal Society of Chemistry.
- 7. McEwen, F.L. and G.R. Stephenson. 1979. The use and significance of pesticides in the environment. NY: John Wiley and Sons, Inc.
- 8. Morse, R. A. 1987. Bee poisoning. In 1988 New York State pesticide recommendations. Forty-ninth annual pest control conference. Nov. 9, 10, 11. Cornell University, Ithaca, NY.
- 9. Occupational Health Services, Inc. 1986. Material safety data sheet. Secaucus, NJ: OHS, Inc.
- 10.U.S. Environmental Protection Agency. 1988. Personal communication with Vicky Walter. Office of Pesticide Programs, Regulatory Division. PM-25. Washington, DC.
- 11.\_\_\_\_. 1987 (Feb.). Environmental News. Office of Public Affairs (A-107). Washington, DC.
- 12.\_\_\_\_. 1985 (June 30). Chemical fact sheet for metribuzin. Fact sheet no. 53. Washington, DC.
- 13.\_\_\_\_\_. 1984. Memorandum from Stuart Z. Cohen, Ph.D. List of potential groundwater contaminants. Office of Pesticides and Toxic Substances. Washington, DC. Photocopy.
- 14. Weed Science Society of America. 1983. Herbicide handbook. Fifth edition. Champaign, IL: WSSA, Herbicide Handbook Committee.
- 15. Worthing, C. R., ed. 1983. The pesticide manual: A world compendium. Croydon, England: The British Crop Protection Council.
- 16. DuPont. 1991. Material Safety Data Sheet for Metribuzin Technical.

Du Pont, Registration and Regulatory Affairs, Wilmington, DE.

17. Meister, R.T. (ed.). 1992. Farm Chemicals Handbook '92. Meister Publishing Company, Willoughby, OH.

- 18. US EPA. 1988 (Aug.). Metribuzin: Health Advisory. Office of Drinking Water, US EPA, Washington, DC.
- 19. USDA SCS. 1990 (No). SCS/ARS/CES Pesticide Properties Database: Version 2.0 (Summary). USDA Soil Conservation Service, Syracuse, NY.
- 20. Occupational Health Services, Inc. 1991 (May 1). MSDS for metribuzin. OHS Inc., Secaucus, NJ.
- 21. WSSA Herbicide Handbook Committee. Herbicide Handbook of the Weed Science Society of America, 6th Ed. WSSA, Champaign, IL. 1989.