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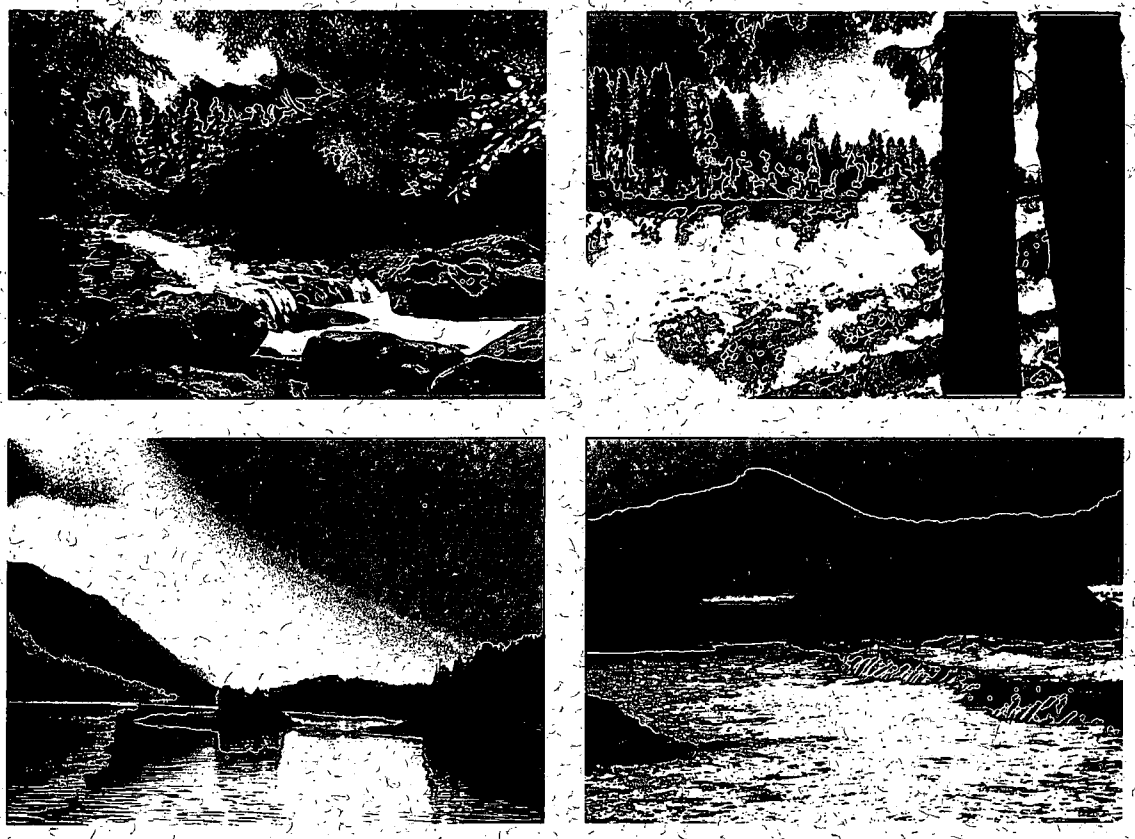
Canadian Water Quality Guidelines for Metribuzin

B.D. Pauli, R.A. Kent and M.P. Wong



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INLAND WATERS DIRECTORATE
WATER QUALITY BRANCH
OTTAWA, ONTARIO, 1990

(Disponible en français sur demande)

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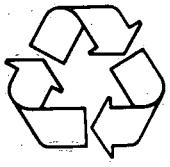

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Abstract

A review of the literature concerning the uses, sources to the environment, environmental fate and behaviour, and toxicity of the triazine herbicide metribuzin and its effects on raw drinking water supply, freshwater aquatic life, agricultural water uses, recreational water quality and aesthetics, and industrial water supplies were examined, From the information summarized in this report, guidelines for metribuzin were formulated for the protection of these specific water uses.

Résumé

On a examiné les documents portant sur l'utilisation l'introduction dans l'environnement, l'evolution et le comportement dans le milieu et la toxicité de la métribuzine, un herbicide de la famille des triazines. On a examiné aussi les questions suivantes : la présence de la métribuzine dans l'approvisionnement en eau potable, ses effets sur les organismes aquatiques d'eau douce et sur l'utilisation de l'eau dans l'industrie et dans l'agriculture ainsi que sur la qualité de l'eau pour les loisirs et l'esthétique. Grace aux renseignements résumés dans ce rapport, des recommandations sont formulées relativement à la métribuzine afin d'assurer la protection de l'eau pour les différentes utilisations mentionnées.

Canadian Water Quality Guidelines for Metribuzin

B.D. Pauli, R.A. Kent, and M.P. Wong

SOURCES, OCCURRENCE, AND CHARACTERISTICS

Uses and Production

Metribuzin is the common name for the triazine herbicide 4-amino-6-*tert*-butyl-3-methylthio-1,2,4-triazin-5(4H)-one (IUPAC) or 4-amino-6-(1,1-dimethylethyl)-3-(methythio)-1,2,4-triazin-5(4H)-one (CAS). The structural formula for metribuzin is found in Figure 1. Its Chemical Abstracts Service Registry Number is 21087-64-9. Trade names include Sencor, Lexone, Sencor Srayule, and Metribuzine.

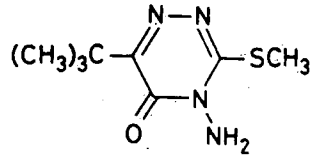

Figure 1. Structural formula for metribuzin.

Metribuzin is a member of the triazine family of herbicides formally known as the triazinones (Hatzios and Penner 1988). It is a selective herbicide used for broadleaf and grass weed control in a variety of crops including potatoes, established alfalfa, barley, grain sorghum, established asparagus, tomatoes, soybeans, canola, citrus, corn, carrots, lentils, lucerne, dry field beans, established cereals and peas, and some range and pasture grasses (Diawara and Banks 1990; Ontario Ministry of Agriculture and Food 1988; Hatzios and Penner 1988; Worthing and Walker 1987; Weed Science Society of America 1983; Smith et al. 1982). Of the total metribuzin used in the United States, 94% is applied to soybeans, and about 1.8%, 1.5%, and 1.2% are used on potatoes, wheat, and sugarcane, respectively (U.S. EPA 1985). Current Canada-wide usage figures are not available.

Metribuzin was developed by Bayer in 1966 (Hatzios and Penner 1988). It was first introduced in 1969 and was field tested and developed by the Mobay Chemical Corporation and E.I. duPont de Nemours in the United States and Canada (Weed Science Society of America 1983). Metribuzin was registered for use in Canada in 1971 by Chemagro, a division of Baychem Corporation (Agriculture Canada 1989). Metribuzin is also involved in the synthesis of isomethiozin, a pro-herbicide that is readily hydrolyzed to the phytotoxic metribuzin once it enters susceptible plants (Hatzios and Penner 1988). An ethylthio-analogue of metribuzin (ethyl-metribuzin or SMY 1500) has recently been developed for grass control in winter wheat (Peek and Appleby 1989). This metribuzin analogue has Chemical Abstracts Service (CAS) Registry Number 64529-56-2 and a CAS nomenclature formula of 4-amino-6-(1,1-dimethylethyl)-3-(ethylthio)-1,2,4-triazin-5(4H)-one (Ratliff and Peeper 1987); the proposed common name is ethiozin (Fedtke and Schmidt 1988). This compound has been developed because metribuzin has a relatively narrow range of selectivity in winter wheat and restrictions are imposed on its usage because of wheat growth stage, varietal tolerance, and soil and environmental factors (Peek and Appleby 1989).

Metribuzin is formulated as a wettable powder and is applied during the pre-plant, preemergence, or postemergence stages. Application rates vary from 0.25 to 4 $kg \cdot ha^{-1}$ (Smith et al. 1982) for crops, while applications to railroad rights-of-way in the United States range from 6.0 to 8.0 $kg \cdot ha^{-1}$ (U.S. EPA 1988). For crops, the soil texture may affect the application rate (Peek and Appleby 1989). Metribuzin may be soil-incorporated, soil-surface applied, or applied foliarly. It can be applied with broadcast or band (row) applications using ground equipment; in the United States, it can also be applied by aerial spraying or sprinkler irrigation (U.S. EPA 1985). Metribuzin is also available as a flowable concentrate and as a dry flowable formulation.

Minor uptake of metribuzin by plants occurs through the foliage when metribuzin is applied postemergence, but the major route is through the roots. The basis for plant tolerance and selectivity is herbicide degradation by resistant species (Ontario Ministry of Agriculture and Food 1988). Metribuzin may enter into synergistic relationships with residues from previously applied herbicides (e.g., atrazine) or may be applied in tank-mixtures with other herbicides to increase its phytotoxicity (Diawara and Banks 1990; Pawlak et al. 1987; Friesen and Wall 1986; Ladlie et al. 1977a, 1977b).

In Ontario, use of metribuzin has been continuously increasing. In 1978, almost 60 metric tonnes (t) of metribuzin were applied to field crops, fruits, vegetables, and roadsides; in 1983 over 200 t were used; in 1988, over 258 t were used (Roller 1979; McGee 1984; Moxley 1989). In Prince Edward Island, 4320 kg of the active ingredient (ai) of metribuzin were sold in 1986. In Nova Scotia, 370 kg-ai were sold the same year (Seatech Investigation Services Ltd. 1988). In New Brunswick, 2537 kg of metribuzin were sold in 1987 (Shanks 1988) compared to 2461 kg sold in 1986 (Shanks 1987). Specific data on the use of metribuzin in Quebec were not found, however, Reiss et al. (1984) reported that the triazine/triazole class of herbicides, which includes metribuzin, had sales of over 577 t in Quebec in 1982.

Canadian importation data for metribuzin in 1986 and 1987 were not available as this compound was not individually listed by Statistics Canada during those years.

Chemical and Physical Properties

Metribuzin is designated an *as*-triazine (asymmetrical triazine) because of the asymmetrical orientation of the nitrogens on the triazine ring.

The physical and chemical properties of metribuzin are summarized in Table 1. Metribuzin is a solid at standard temperature and pressure and is characterized by a low vapour pressure and octanol/water partition coefficient, and a high water solubility (aqueous solubility is 1200 $mg \cdot L^{-1}$ at 20°C) (Worthing and Walker 1987). The compound is a heterocyclic, basic organic molecule that protonates and ionizes in acidic aqueous solutions, forming cationic species; at normal soil pH levels the compound should exist as only the molecular species (Weber 1980). The parent compound metribuzin can degrade to three different metabolites: DA (deaminated metribuzin, pK_a = 7.3), DK (diketo metribuzin, pK_a = 10.0), and DADK (deaminated diketo metribuzin, pK_a = 8.3) (Hatzios and Penner 1988). The CAS nomenclature formula for DA is 6-(1,1-dimethylethyl)-3-(methylethyl)-3-(methylthio)-1,2,4-triazin-5-(4H)-one; for DK, 4-amino-6(1,1-dimethylethyl-1,2,4-triazin-3,5-(2H, 4H)-dione; and for DADK, 6-(1,1-dimethylethyl)-1,2,4-triazin-3,5-(2H,4H)-dione (Albro et al. 1984). The CAS Registry Number for DK is 56507-37-0; for DA, 35045-02-4; and for DADK, 52236-30-3. The metabolite DK results from a hydrolytic demethylthiolation of the parent compound, which in turn can be deaminated to DADK, a terminal, non-phytotoxic metabolite (Hatzios and Penner 1988).

Table 1. Physical and Chemical Properties of Metribuzin

Chemical formula	$C_8H_{14}N_4OS$
Physical state	crystalline solid[1]
Colour	colourless[1]
Molecular weight	214.3[1]
Specific gravity	1.28[2]
Melting point	125.5°C–126.5°C[1]
Boiling point	not determined
Vapour pressure (20°C)	<1.3 mPa[1]
Aqueous solubility (20°C)	1200 $mg \cdot L^{-1}$[1]
	1220 $mg \cdot L^{-1}$[2]
Solvent solubility (20°C):	
acetone	820 $g \cdot kg^{-1}$[1]
benzene	220 $g \cdot kg^{-1}$[1]
chloroform	850 $g \cdot kg^{-1}$[1]
ethanol	190 $g \cdot kg^{-1}$[1]
hexane	2 $g \cdot kg^{-1}$[1]
toluene	120 $g \cdot kg^{-1}$[1]
cyclohexanane	1000 $g \cdot kg^{-1}$[1]
K_{ow} (estimate)	(log P_{ow}) 1.87[3]

[1] Worthing and Walker (1987)
[2] Weed Science Society of America (1983)
[3] Banerjee et al. (1980)

The pK_a of metribuzin has been reported to be 1.1 (Weber 1980) or 1.0 (Albro et al. 1984) by spectrophotometric titration and 7.1 by potentiometric titration (Albro et al. 1984). Albro et al. (1984) concluded that the spectrophotometric titration could not detect a structural alteration (monomerization) occurring at pH 7.1, and that the pK_a value of 1.0 determined spectrophotometrically may involve acid-

catalyzed decomposition of the metribuzin rather than just protonation. The potentiometrically determined pK_a did not simply correspond to protonation of the amino group. In a review published in 1988, Hatzios and Penner cited both of these pK_as, but placed the 1.0 value in their table of physical and chemical properties of metribuzin. Peek and Appleby (1989) list a pK_a of 7.3 for metribuzin, but do not mention how they arrived at this value.

In Canada, metribuzin is available as the technical grade product (90% ai) from Chemagro Ltd.; as commercial wettable powder formulations containing 50% ai (Sencor 50 from Chemagro and Lexone from duPont) or 75% ai (Sencor 75%WP from Chemagro); as a dry flowable formulation of 75% wettable granules (Lexone DF and Sencor 75DF); as 50% soluble granules (Sencor 50); or as a flowable suspension containing 42.1% (480 $g \cdot L^{-1}$) metribuzin (Lexone L from duPont) or 500 $g \cdot L^{-1}$ (Sencor 500F from Chemagro) (Agriculture Canada 1989). Mobay has also introduced a 75% water-dispersable granular formulation called Sencor Sprayule (Hatzios and Penner 1988). Along with the technical product, a number of adjuvants have been tested in attempts to develop a formulation with reduced phytotoxicity to crops without loss of weed control (Street et al. 1987).

Mode of Action

Metribuzin is a photosynthesis inhibitor (Fedtke 1972; Machado et al. 1978; Selim et al. 1989). Büchel (1972) and Draber et al. (1974) reported that metribuzin interrupts a critical step in the Hill reaction of photosynthesis. Klepper (1975) has suggested that metribuzin may have a secondary mode of action by inhibiting nitrite reduction in plant cells. Fedtke (1979) argued against nitrogen metabolism interference as a mode of action of metribuzin, and noted that the molecular site of the inhibition of photosynthesis is located between the primary and secondary electron acceptor of Photosystem II. McEwen and Stephenson (1979) also reported that metribuzin inhibits the electron transport system of photosynthesis.

After soil application, metribuzin is taken in at the roots of plants, translocated upward in the xylem, and moved distally to concentrate in the stems and leaves. Metribuzin can also be absorbed through the leaf cuticle from a postemergence application. Treated plants are subjected to carbohydrate stress related to diminished photosynthetic electron transport. The decrease in CO_2 assimilation and carbohydrate synthesis leads to starvation of the plants as energy-requiring processes continue (Hatzios and Penner 1988). Fedtke (1979) reported that the response of tolerant soybean plants to sublethal concentrations of metribuzin was similar to that occurring with exposure to low light intensities; the observed responses indicated a shade adaptation that was mostly related to decreased CO_2 fixation. Tolerance to metribuzin is also attributed to rapid detoxification of the parent compound in resistant crop species (Mangeot et al. 1979).

Methods of Analysis

Methods for the analysis of metribuzin in water and sediment include dual-column capillary gas chromatography (GC) with nitrogen-phosphorus thermionic specific detection (detection limit 0.1 $\mu g \cdot L^{-1}$) (Richards et al. 1987) and high-performance liquid chromatography (HPLC) (detection limit 5 $\mu g \cdot L^{-1}$) (Brown et al. 1984). The standard analysis of metribuzin using GC is described by U.S. EPA Method 633 and includes a solvent extraction with methylene chloride and measurement with a thermionic bead detector (detection limit of 0.46 $\mu g \cdot L^{-1}$ for metribuzin in water samples) (U.S. EPA 1987). A GC electrolytic conductivity detector has been used to analyze water samples for metribuzin (Frank and Logan 1988). Additional methods used for the quantification of metribuzin and its metabolites in plant tissues, soil samples, or water are outlined in Hatzios and Penner (1988) and Weed Science Society of America (1983). Shaw et al. (1985) have used a chlorophyll fluorescence bioassay to examine metribuzin residues in soil. Recently, Selim et al. (1989) used a bioassay that measured the inhibition of oxygen evolution in the Eurasian watermilfoil (*Myriophyllum spicatum*) to detect a metribuzin concentration of 10^{-7}M ($\approx$ 11 $\mu g.L^{-1}$) in a culture medium and in raw lake water.

Entry into the Environment

Since metribuzin is used exclusively as a herbicide, its entry into the environment may occur through its use as such or through its misuse (for instance, spills). The translocation of metribuzin to surface waters could result from accidental discharge or direct application to watercourses, from spray and vapour drift, from precipitation, or from surface runoff and ground-water intrusions from treated lands. In general, losses of soil-applied triazine herbicides, including metribuzin, primarily occur through movement in the water phase of soil runoff as opposed to translocation with eroded soil sediment (Glotfelty et al. 1984).

Table 2. Metribuzin Residues in Runoff from Agricultural Land

Plot description (soil type/crop)	Formulation (% ai)	Application rate	Method of application	Residues in runoff and days posttreatment	Reference
Pullman, Washington, winter wheat, various tillage practices, silt loam, steeply sloped runoff plots, 20%–26% grade	—	0.45–0.56 kg·ha^{-1}	Fall surface application, hand spray.	44 μg·g^{-1} after 131 d (maximum reported) 3440 μg·g^{-1} in sediment after 130 d (maximum reported) Total field losses through runoff: 1978–1979—3.2% to 5.2% (includes metabolite DADK) 1979–1980—0.04% to 0.5% 1981–1982—0.01% to 1.1%	Brown et al. 1985.
Mississippi Delta field	—	0.56 kg·ha^{-1}	Wettable powder, surface application. Rainfall to runoff ratio 2.60:1.77 (cm).	Mean concentration = 53 μg·g^{-1} 4 d after application	Wauchope et al. 1977; Wauchope and Leonard 1980.
	—	0.56 kg·ha^{-1}	Wettable powder, surface application. Rainfall to runoff ratio 2.40:1.11 (cm).	Mean concentration = 15 μg·g^{-1} 9 d after application	
Stoneville, Mississippi, 0.2 ha, 0.5% slope, sandy loam, soybeans	—	0.56 kg·ha^{-1}	Wettable powder, surface application.	2.1% lost by means of runoff after 1 month	Wauchope 1978.
	—	0.56 kg·ha^{-1}	Wettable powder, surface application.	0.9% lost by means of runoff after 5 months	

Runoff events occurring within 2 weeks of soil application are the most important with respect to delivery to watercourses (see Table 2). On average, however, annual losses of soil-applied triazine herbicides, including metribuzin, are generally 3% or less of that applied (Baker 1985; Brown et al. 1985; Glotfelty et al. 1984; Johnson and Baker 1982, 1984). Subsurface drainage would not appear to be a major route for transport of this herbicide to surface waters or drinking water supplies due to its low mobility and relatively nonpersistent nature (Hatzios and Penner 1988; Roberts et al. 1979).

Accidents and spills have also been shown to be an important mechanism for the entry of metribuzin into surface waters. This includes spraying directly into water, emptying tanks, mixing pesticides or cleaning equipment close to water, and seepage from discarded containers (Frank et al. 1982). Frank et al. (1982) conducted a 2-year investigation of pesticide losses from 11 agricultural watersheds in southern Ontario. The watersheds ranged in size from 1860 to 7913 ha, with a total area of 47 072 ha. Approximately 94% of the land was devoted to agricultural production. Spray season loss of metribuzin to the streams draining these watersheds was calculated to be 401 g over a 2-year period from 259 kg of herbicide applied. Forty-four percent of the loss was attributed to storm water runoff and snowmelt events and the remainder to spills, spray drift, and direct application to streams. The mean unit-area loss to streams draining the watersheds was 4 and 9 $mg \cdot ha^{-1}$ per annum during the years 1975–1976 and 1976–1977, respectively. The loss to use ratio (the ratio of rate of loss to rate of application) was calculated to be 0.00053 for 1975–1976.

The effect of crop management techniques on metribuzin residues in winter wheat was evaluated by Brown et al. (1985). Soil and runoff losses were generally lower from no-till plots than from tilled plots. The highest concentrations of metribuzin in sediments were associated with runoff events from frozen fields during spring surface thaw. Winter losses of metribuzin plus DADK were as high as 5.2% of the amount applied (23.5 $g \cdot ha^{-1}$) from the very steep runoff plots monitored (20%–26% slope), but typically were 1% or less. The maximum concentration of metribuzin reported in filtered runoff water was 44 $\mu g \cdot L^{-1}$, which occurred during a runoff event 131 d after metribuzin application. In runoff sediment, the maximum concentration of metribuzin was 3440 $\mu g \cdot L^{-1}$ 130 d after metribuzin treatment.

Ground-water recharge includes the water entering the soil profile and leaving the plant root zone. While soluble herbicides such as metribuzin may be leached through soil to contaminate ground water, there is little information on the presence of these compounds in ground water. Metribuzin was applied postemergence at a rate of 0.56 $kg \cdot ha^{-1}$ to tile-drained clay and loamy sand soil planted to corn in Quebec (Muir and Baker 1976). Tile-drain depth was 1 to 1.6 m, with a slope of 0.35%. Metribuzin residues in the tile-drain water ranged from <0.01 $\mu g \cdot L^{-1}$ (below the detection limit) to 1.65 $\mu g \cdot L^{-1}$, with a mean concentration of 0.55 $\mu g \cdot L^{-1}$, for July of 1974 (date of application was 12 June 1974). A mean residue loss rate of 0.07 $g \cdot ha^{-1}$ was calculated for the subsurface tile drainage for July.

The movement of pesticides and soil from fields in an Iowa watershed was studied for 5 years by Johnson and Baker (1982, 1984). Metribuzin was applied without soil incorporation immediately after planting at a rate of 0.56 $kg \cdot ha^{-1}$ using a broadcast sprayer. Soybeans were planted on the conventionally tilled plots. Field-border soil samples and stream water and sediment samples were taken to assess herbicide loss during and after application. Loss during application was low, as the amount of herbicide reaching filter paper disks on the soil surface was equivalent to the amount leaving the sprayer nozzle. During 1976 to 1978, however, soil analyses immediately following application indicated a large percentage loss of herbicide within 2–4 h of application. The same loss did not occur in 1979 and 1980, but the authors did not speculate on the reasons for this discrepancy. These studies suggested, however, that volatilization is not a major fate process for metribuzin as soil sampling indicated that herbicide levels in dry soil did not decrease significantly before the first rainfall. In 1979, above average rainfall, runoff, and erosion resulted in metribuzin runoff losses as high as 7.2%. In contrast, from 1976 to 1978, metribuzin losses never exceeded 1% of the amount applied. In 1980, field loss of metribuzin returned to approximately 1%. Most of the metribuzin was lost in the runoff water; in 1979, 82.8% of the annual loss was associated with the water phase, while in 1980 the amount in water was 97.0%. Although little metribuzin was lost with sediment, concentrations in sediment were 2 to 10 times greater than the concentrations in an equivalent amount of water. Although metribuzin did not readily leach below the 15-cm depth, field sampling indicated that metribuzin did not build up during 3 years of successive application, and that by late July or August

soil concentrations were below the detection limit (detection limit not given) (Johnson and Baker 1984).

In a simulation study, Donigian and Carsel (1987) found that in-stream concentrations of pesticides in runoff water were reduced by the implementation of either reduced or no-till practices. From the results of their simulation, these authors found that ground-water concentrations of metribuzin would be low after a 1.0-kg·ha^{-1} application, with predicted maximum ground-water concentrations below expected detection limits (approximately 0.51 ng·L^{-1}). However, they admitted to some uncertainty with the data and the original parameters entered into the model.

Brown et al. (1984) investigated metribuzin and DADK in runoff waters collected downslope from wheat plots treated with metribuzin. Samples were taken from collection tanks at the base of the plots within 24 h of the cessation of the runoff event. After a minor runoff event 65 d after metribuzin treatment, DADK was detected in the collection tanks at 5.7 μg·L^{-1} and metribuzin at 14.1 μg·L^{-1}. Following a major runoff event 128 d after application, metribuzin was found at 6.3 μg·L^{-1} and DADK at 3.3 μg·L^{-1}.

One further path through which metribuzin can enter the environment is atmospheric deposition. Richards et al. (1987) analyzed rainwater samples collected from four stations in the north-central United States during the spring and summer of 1985. They found metribuzin in 21 and 24 of the 30 rainwater samples taken from two of the stations, but concentrations were less than 0.1 μg·L^{-1}. The presence of metribuzin in the rainwater was highly seasonal, with the highest concentrations occurring after herbicide application in April and May. The authors speculated that the atmospheric life of metribuzin is short, and that replenishment of the atmospheric pool probably involves volatilization and wind erosion of soil particles with adsorbed metribuzin; an alternate route of atmospheric entrainment during application is probably of minor consequence. The authors concluded that atmospheric deposition of metribuzin is not expected to be detrimental to plants as the measured concentrations in precipitation were low.

Concentrations in Water, Sediment, and Biota

Data on the concentrations of metribuzin in Canadian surface and ground waters are summarized in Appendix A. Frank et al. (1979) reported a concentration of 0.4 μg·L^{-1} in water samples from the mouth of the Ruscum River (at Lake St. Clair), Ontario, in July 1977. None of the other 91 streams flowing into the Great Lakes sampled during the study contained detectable metribuzin concentrations (detection limit 0.03 μg·L^{-1}). Of the 45 suspended solids samples collected during 1974–1976 by Frank et al. (1979), no metribuzin was detected (detection limit 0.05 μg·L^{-1}).

Between January 1981 and December 1985, Frank and Logan (1988) studied pesticide loadings in three rivers (the Grand, Saugeen, and Thames) draining three major agricultural watersheds in southwestern Ontario. In 1983, 11.74 t and 34.77 t of metribuzin were applied to the Grand and Thames river basins, respectively. The Grand River basin contained 460 690 ha of farm land, while the Thames River basin had a total of 601 649 ha as crop land. Of the 297 water samples collected at the river mouths of these two basins between 1981 and 1985, only 6 (2.0%) had detectable concentrations of metribuzin (detection limit <0.02 μg·L^{-1}).

Roberts et al. (1979) detected metribuzin in 16 of 360 (4.4%) water samples collected in 1973–1974 during an intensive survey of a small agricultural basin draining into Lake Erie in southwestern Ontario. Application of metribuzin was 41.5 kg in 1973. In 1974, 170 ha of soybeans, potatoes, and tomatoes were treated with 122 kg of metribuzin (0.718 kg·ha^{-1}). The maximum reported concentration of metribuzin in the water was 22 μg·L^{-1} in early June (Appendix A). Residues were detected in the water only during the May to July spray period (detection limit <0.1 μg·L^{-1}).

Ripley et al. (1986) examined pesticide contamination of 291 farm wells in Ontario and analyzed 1843 water samples for the presence of triazine herbicides. Ten (3.4%) wells contained metribuzin at concentrations above 1 μg·L^{-1}, while two wells contained metribuzin in concentrations above 60 μg·L^{-1}. The authors noted that their data may have been biased as a result of their selection of shallow wells in sandy soil near areas of heavy pesticide use.

In a more recent study of farm-well contamination by pesticides in southern Ontario, Frank, Ripley, et al. (1987) reported that only 1 well of 91 surveyed contained detectable residues of metribuzin (detection limit 0.1 μg·L^{-1}). Sixteen of the 91 farms had used metribuzin the preceding year, and the farms were on

mineral soils in areas of heavy pesticide use. The contamination in the single well was attributed to spills in the vicinity of the well. The initial concentration was 42 $\mu g \cdot L^{-1}$. Decontamination efforts helped reduce this concentration to less than 2 $\mu g \cdot L^{-1}$ after about 8 months (Appendix A). The authors concluded that there was no evidence that normal field application of metribuzin resulted in its leaching to the ground water and contaminating wells. However, low level contamination may result from surface runoff entering wells.

Frank, Clegg, et al. (1987) reported the incidence of pesticide contamination in 160 rural wells surveyed in Ontario between 1979 and 1984. On-site investigations were undertaken in 311 instances where well contamination was suspected. Metribuzin (detection limit 0.1 $\mu g \cdot L^{-1}$) was not found in any of the 112 wells investigated for potential surface runoff and spray drift contamination. Metribuzin was detected in 2 of 48 wells investigated for contamination by spills. Maximum concentrations were 187 $\mu g \cdot L^{-1}$ (for a container spill directly into the well), and 59 $\mu g \cdot L^{-1}$ for a well contaminated by overfilling, emptying, or rinsing spray equipment near the well. Decontamination efforts by pumping out the water in these wells helped reduce the concentrations to about 2 $\mu g \cdot L^{-1}$ after 4 months.

In 1983, no metribuzin was found in 14 surface-water samples (detection limit 0.14 $\mu g \cdot L^{-1}$), 27 sediment samples (detection limit 0.014 $mg \cdot kg^{-1}$), or 37 fish muscle samples (detection limit 0.04 $mg \cdot kg^{-1}$) collected in New Brunswick (Bailey 1985). Fish species included longnose sucker, white sucker, lake whitefish, speckled trout, yellow perch, brown bullhead, and landlocked salmon. In 1986, metribuzin was not detected in 23 surface-water and 27 sediment samples, although the detection limit for metribuzin in water had been lowered to 0.03 $\mu g \cdot L^{-1}$ (O'Neill and Bailey 1987). In 1987, 112 subsurface drainage water samples were analyzed at a detection limit of 0.01 $\mu g \cdot L^{-1}$ and metribuzin was found in 16 (maximum concentration of 0.02 $\mu g \cdot L^{-1}$). When a further 11 samples were analyzed at a detection limit of 0.001 $\mu g \cdot L^{-1}$, all 11 samples showed metribuzin contamination. The maximum concentration was again 0.02 $\mu g \cdot L^{-1}$ (O'Neill et al. 1988). In Alberta, between 1984 and 1988, 37 surface-water samples were analyzed (detection limit 0.03–0.15 $\mu g \cdot L^{-1}$), but no metribuzin was detected (Alberta Environment Centre, unpub. data). In Prince Edward Island in 1985, 12 water samples were analyzed for metribuzin with a detection limit of 0.16 $\mu g \cdot L^{-1}$, and a further 10 samples were analyzed with a detection limit of 0.04 $\mu g \cdot L^{-1}$. No metribuzin was found in any of the samples (Clair et al. 1987). In Quebec, a maximum concentration of 19.8 $\mu g \cdot L^{-1}$ metribuzin was found in ground water (I. Giroux, 1990, Ministère de l'environnement du Québec, pers. com.).

Metribuzin was found in the influent of three water treatment plants collecting storm runoff in northwestern Ohio (Miltner et al. 1988). The Maumee River (draining a watershed of 1.6 million ha) was sampled on 20 d during May, June, and July of 1984, and detectable residues of metribuzin were found on 16 d (with a mean concentration of 1.25 $\mu g \cdot L^{-1}$ and a maximum concentration of 4.90 $\mu g \cdot L^{-1}$). The Sandusky River, which drains an area of 324 009 ha, contained metribuzin on 18 of 19 sampling days with a mean concentration of 1.82 $\mu g \cdot L^{-1}$ and maximum of 6.03 $\mu g \cdot L^{-1}$. In 1982, metribuzin was found in the Sandusky River in concentrations above 8.0 $\mu g \cdot L^{-1}$ during runoff events (Baker 1985).

The U.S. EPA (1987) reported metribuzin in 1517 of 3580 surface-water samples and in 54 of 240 ground-water samples from 14 different states. The highest concentration found in surface water was 22.8 $\mu g \cdot L^{-1}$, and the maximum concentration in ground water was 1.25 $\mu g \cdot L^{-1}$. Metribuzin was also found in three observation wells in northern Iowa at concentrations ranging from 0.09 to 4.35 $\mu g \cdot L^{-1}$ (Cohen et al. 1986).

Wnuk et al. (1987) studied public drinking water supplies in Iowa that used surface water (rivers, lakes, and reservoirs) as a water source. Treated and untreated water was collected following rainfall in the late spring or early summer. In 1982, 1 of 15 untreated water samples had detectable levels of metribuzin (0.89 $\mu g \cdot L^{-1}$). Water samples that had already been passed through municipal water treatment plants contained metribuzin in 4 of 33 (12%) samples. Concentrations in the treated water ranged from 0.14 to 0.45 $\mu g \cdot L^{-1}$, with a mean of 0.29 $\mu g \cdot L^{-1}$ (detection limit 0.1 $\mu g \cdot L^{-1}$).

Finally, Arruda et al. (1988) found metribuzin in 1 of 7 water samples (concentration of 0.33 $\mu g \cdot L^{-1}$; no detection limits given) in a lake in an agricultural watershed along the Kansas-Nebraska border.

Environmental Fate, Persistence, and Degradation

Soil

The persistence of triazine herbicides in Canadian soils, as determined by both laboratory and field investigations, was summarized by Smith (1982, 1985). Metribuzin carry-over (persistence of detectable residues over time) after 5 months ranged from 0% to 20% of the amount applied in field persistence studies in Saskatchewan, Manitoba, Ontario, and Prince Edward Island. Marriage et al. (1978) reported about 10% of an initial 1.12-kg·ha^{-1} application was recovered after 12 weeks from a clay loam soil in Ontario. Webster and Reimer (1976b) reported that $<10\%$ remained at the end of the growing season after application of 2 kg·ha^{-1} to a fine sandy loam in Manitoba. Smith and Hayden (1982) reported that $<2\%$ to 20% was recovered 22 weeks after an application of 1 kg·ha^{-1} metribuzin to clay, clay loam, and sandy loam soil in Saskatchewan. Smith (1985) concluded that metribuzin was less persistent than atrazine and simazine, but more persistent than cyanazine.

In field tests, metribuzin dissipates with a half-life of less than 6 months (Table 3); its half-life in surface soils is approximately 20-50 d (Bouchard et al. 1982; Hyzak and Zimdahl 1974; Ladlie et al. 1976c; Pettygrove and Naylor 1985; Savage 1977). Soil characteristics, chemical formulation, or application rate do not significantly affect the dissipation rate (U.S. EPA 1987), while depth in the soil is correlated with increasing persistence (Moorman and Harper 1989).

Although some nonbiological degradation occurs, microbial metabolism appears to be the major pathway for the removal of metribuzin from soil. Soils sterilized with irradiation (Sharom and Stephenson 1976), chemicals (Ballerstedt and Banks 1982; Ladlie et al. 1976b), or autoclaving (Savage 1977; Bouchard et al. 1982) all had reduced rates of loss of metribuzin relative to non-amended soils. On the other hand, enrichment of soils with glucose (Savage 1977; Pettygrove and Naylor 1985) tended to increase metribuzin degradation rates, further implying that microbial activity is an important dissipation pathway.

No reports were found to suggest that there is a buildup in the soil of microorganisms effective in metribuzin degradation after repeated applications of the herbicide. Kaufman and Kearney (1970) reported that an increase in the ability of the soil system to inactivate herbicides fails to occur with the *s*-triazines. Sheets and Danielson (1960) reported that, rather than an increase in the ability of the soil system to inactivate the *s*-triazines, the soil retains the same ability over a long period of time. Duke (1964), however, reported that there was some microbial adaptation and enrichment processes occurring during a study of the microbial degradation of ametryne, a related methylthio-*s*-triazine.

Sharom and Stephenson (1976) demonstrated that after 6 months incubation in a silt loam soil, the degradation products of ^{14}C-labelled metribuzin included 20% DK, 20% DA, and 50% DADK. Ten percent of the radioactivity was identified as unaltered metribuzin. The heterocyclic ring of metribuzin can also be cleaved by microbial action (Hatzios and Penner 1988).

Allen and Walker (1987) examined the influence of soil properties on the rates of metribuzin metabolism in laboratory experiments. Metribuzin was applied to the soils at a rate of 700 g-ai·kg^{-1}. Metribuzin degradation was closely related to microbial activity and the availability of the herbicide in the soil solution (between 12% and 32% of the metribuzin was present in the water phase). Degradation rate constants for metribuzin were significantly correlated with the amount of the herbicide available in the soil solution, the Freundlich adsorption coefficient, the clay, sand, and organic matter content of the soil, and the available potassium. The latter correlation was probably due to the close correlation between soil potassium and microbial activity. Further experiments by Allen and Walker (1988) supported the importance of microbial activity by showing that rates of metribuzin degradation in two soils were diminished when three different microbial inhibitors were added to the soil.

In Saskatchewan, Smith and Walker (1989) examined the rate of metribuzin loss from a Regina heavy clay under different laboratory-controlled moisture and temperature conditions. At the same time, the persistence of metribuzin was examined in the same soil in a field study. In the laboratory, metribuzin at 2.0 μg·g^{-1} was added to the soil (70% clay, 25% silt, 5% sand, 4.2% organic carbon content), which was then incubated at different moisture conditions and temperatures (see Appendix B). Metribuzin breakdown followed first-order kinetics. The half-life increased with decreasing soil moisture content and temperature. Laboratory half-lives at 25°C ranged from 28 d at field capacity moisture (40%) to above 300 d at 8% soil moisture content. At 34% soil

Table 3. Summary of Metribuzin Degradation in Soil/Sediment and Water

Pathway	In soil/sediment	In water
Photolysis	— some occurs[1] but insignificant under field conditions[2]	— not a major path of loss; possible sensitized photochemical degradation[3]
Oxidation	— no data	— no data
Aerobic metabolism	— major degradative pathway[2][4][5][6] — major metabolites: deaminated metribuzin diketo metribuzin deaminated-diketo metribuzin[6]	— slow microbial degradation in water[3] — major metabolites: no data
Anaerobic metabolism	— little occurs[1][7]	— no data
Volatilization	— insignificant under field conditions[2]	— not a major fate process[3]
Mobility	— moderately mobile depending on soil texture; more mobile in coarse soils[1][2] — little leaching in soils with high organic matter[8] — readily leached in sandy soils[1][9] — low concentrations in runoff[10][11][12]	
Adsorption/desorption	— related to organic matter, clay, and moisture content[5] — decreases with increasing pH[2] K_d = 0.27 sandy soil[1] 3.41 clay soil[1] 7.00 silty clay loam[13] — no sediment data	
Persistence	$t_{1/2}$ = <6 months[1] 7–28 d (min.)[2] 14–28 d under ideal conditions[2] about 2 months during growing season[2] 35–63 d in silt loam and sandy loam[1] 20–50 d[14]	$t_{1/2}$ = 2.5–6.5 d[1][15]

[1] U.S. EPA 1987.
[2] Weed Science Society of America 1983.
[3] Muir 1990.
[4] Allen and Walker 1988.
[5] Savage 1977.
[6] Sharom and Stephenson 1976.
[7] Peter and Weber 1985.
[8] Jarczyk 1972.
[9] Smith and Willis 1985.
[10] Brown et al. 1985.
[11] Wauchope and Leonard 1980.
[12] Wauchope 1978.
[13] Peek and Appleby 1989.
[14] Moorman and Harper 1989.
[15] Shaw and Flint 1971.

moisture, the half-life was 22 d at 30°C, increasing to 193 d at 5°C. In the field, the half-life of a 1.0-kg·ha^{-1} metribuzin treatment (applied without incorporation) was approximately 60 d, with about 31% of the herbicide remaining at the end of the growing season 106 d after application. The authors noted that the field half-life may have been unusually long because of the dry conditions occurring during the growing season.

The degradation of metribuzin and its metabolites in a Manitoba fine sandy loam soil were investigated under field conditions by Webster and Reimer (1976b). Metribuzin was applied at rates of 1.0 and 2.0 kg·ha^{-1} at times corresponding to preemergence (mid-June), postemergence (early July), and preharvest (mid-August). Residues measured in the top 5 cm of soil just prior to freeze-up in late October were generally less than 10% of applied amounts irrespective of the application date. Little degradation occurred over the winter months. The maximum concentration of metabolite residues (approximately 1.16 μg·L^{-1}) occurred in mid-July after a 2-week lag period. The metabolite residues in turn degraded quickly and almost completely by early September. By May of the following year, the parent metribuzin compound was present at an average concentration of 0.070 μg·kg^{-1} dry weight of soil, and DK remained at only trace levels.

In the study by Brown et al. (1985) mentioned above, the soil half-life of metribuzin applied in late fall was about 112 d under winter conditions in Washington. Trace amounts of metribuzin and DADK were detected to a depth of 21 cm in the silt loam soil. The metribuzin concentration was 0.11 mg·kg^{-1} in the 0–7 cm soil horizon and 0.026 mg·kg^{-1} in the 7–14 cm soil horizon 192 d following application of 0.43 to 0.56 kg·ha^{-1}. After 192 d, DADK concentrations ranged from 0.013 mg·kg^{-1} to 0.024 mg·kg^{-1} in the upper soil level, and traces were found in the 7–14 and 14–21 cm horizons.

Under aerobic conditions, metribuzin at 10 μg·g^{-1} degraded with a half-life of 35–63 d in silt loam and sandy loam soils treated with a 50% wettable powder formulation of the herbicide (U.S. EPA 1987).

^{14}C-metribuzin degraded with a half-life of 15 d on a silty clay soil exposed to sunlight (unpub. study cited in U.S. EPA 1987); the half-life in samples kept in the dark was 56 d. After 70 d, metabolites in the sunlight-irradiated soil were 20.6% DADK, 6.5% DA, plus 7.0% parent compound. Fifty-six percent of the applied radioactivity was bound to the soil.

The kinetics of metribuzin decomposition in soil were investigated by Hance and Haynes (1981) using laboratory systems. A sandy loam soil (70% sand, 15% silt, 14% clay, 1.3% organic carbon, and pH 6.2) was incubated at 22°C ± 2°C in the dark under four different conditions: as fresh soil incubated in polyethylene bags, as air-dried soil rewetted and incubated in polyethylene bags, as complete soil cores, and using a perfusion apparatus. Metribuzin half-life and time for 90% decomposition was measured. Half-life estimates were calculated using the Michaelis-Menten power rate and first-order kinetics-derived models. Half-life estimates ranged from 11 to 58 d (Michaelis-Menten) and from 6 to 63 d (first-order kinetics) for the four laboratory conditions. Estimates of the time taken for 90% decomposition ranged from 44 to 1007 d for the power rate equations, while the predicted values from the first-order kinetics equations were from 42 to 209 d. The shortest first-order half-life estimate (6 d) was taken from an undisturbed soil core experiment. In general, the test systems indicated that 50% and 90% decomposition would occur within 20 and 50 d, respectively.

Using laboratory experiments with soil samples containing 1.0 mg·kg^{-1} technical metribuzin incubated in the dark at 25°C, Moorman and Harper (1989) studied the degradation and mineralization of metribuzin. Degradation proceeded at a much greater rate in the surface soil (0–10 cm) than in the subsoil; degradation in the surface soil followed a second-order reaction, while degradation was a half-order process in the subsurface soil. The percentage of applied metribuzin remaining after 91 d of incubation was 4% at 0–10 cm, 15.8% at 35–80 cm, and 20.4% at 125–150 cm. The authors noted that the slower reaction rates corresponded with decreased populations of microorganisms in the subsurface horizons. Metribuzin was not readily mineralized; mineralization was a microbial process, but the microbes in the subsurface soil were not able to mineralize the triazinone ring. The authors concluded that due to the reduced microbial activity in the subsoils, a significant portion of metribuzin degradation in the subsurface soils may be due to abiotic processes.

Savage (1977) reported that metribuzin degradation in six different soil types under greenhouse conditions followed first-order kinetics with half-life values ranging from 17 to 28 d. Results of some of the experiments are summarized in Appendix B. The

importance of microbial activity in the degradation of metribuzin was suggested by additional laboratory incubation studies; degradation was more rapid in non-autoclaved field soil and in glucose-enriched soil relative to autoclaved soil or soil that had been air-dried for 1 year. Cucumber bioassays indicated that metribuzin phytotoxicity was lost in clay soils within a few weeks of application and that persistence of the herbicidal activity and herbicide availability depended on soil type (increased organic matter content increased the rate of microbial degradation while at the same time increasing adsorption).

In laboratory studies, Savage (1980) investigated the loss of metribuzin through volatilization and photodecomposition. Volatility losses from soil surfaces approached 10% to 12% of that initially applied for the first few hours following application. Losses decreased thereafter. A decrease in total volatility was noted for an increase in soil moisture from 3% to 30% moisture content. The decrease was attributed to the effects of solubility on the vapour pressure of this relatively soluble herbicide. Irradiation by fluorescent sun lamps (light spectrum not given) of metribuzin applied to glass yielded a half-life of 4 h. Losses of metribuzin applied to soil were lower, although the author reported that 30%–50% losses occurred within 1–2 d. Half-life values of 4–5 d were calculated for metribuzin on the soil surface when exposed to "warm" temperatures and intense irradiation.

Bartl and Korte (1975) also studied photochemical degradation of thin films of metribuzin from glass surfaces in the laboratory. They reported that photochemical degradation only proceeded in the presence of moisture. Their experiments indicated that no further thermodegradation occurred after 20 h at 110°C. Smith et al. (1982) stated that vapour movement should not present a residue problem with metribuzin because the triazine herbicides are relatively non-volatile.

Jensen et al. (1989) conducted a field study in Prince Edward Island to determine whether shade, herbicide incorporation, and crop row width would alter the persistence of metribuzin and contribute to residue carry-over problems. The soils, a fine sandy loam and Berwick loamy sand, received 0.5 $kg \cdot ha^{-1}$ metribuzin, either incorporated with a rake or left on the soil surface. Soybean plants were seeded very closely together on some of the plots, more widely spaced on others, while some plots were left bare to provide variable amounts of canopy cover. On one half of each of the bare, unseeded plots, a wooden cover was erected 15 cm above the soil to provide immediate and permanent cover. The authors state that the increase in persistence resulting from shade and incorporation suggests that photodecomposition and volatility influence metribuzin under field conditions. Further, they conclude that the kinetics of metribuzin degradation in the field follows a two-stage first-order reaction; there is an initial rapid loss occurring immediately after application, possibly influenced by photodecomposition and volatilization, followed by a longer term, less rapid loss—during which microbial degradation is usually of paramount importance—after soil-herbicide equilibrium has been reached (see LaFleur 1980b). Thus the methods of application and the conditions soon after application may be important influences in field persistence. The half-lives provided in this study, however, are unreliable, as the authors state that there may have been nonbiological degradative losses of metribuzin in their samples awaiting analysis, resulting in underestimation of the actual persistence.

The effect of soil pH on microbial degradation, adsorption, and mobility of metribuzin was investigated by Ladlie et al. (1976a). ^{14}C ring-labelled metribuzin was readily degraded in soil over a 12-week period as measured by evolution of $^{14}CO_2$. Treatment of the soil with sodium azide (i.e., sterilization) drastically reduced $^{14}CO_2$ release at both pH 4.6 and 6.7, indicating decreased microbial degradation of the compound. Degradation of metribuzin increased significantly when soil pH was close to neutral; $^{14}CO_2$ evolution increased from 4.6% at pH 4.6 to 17.9% at pH 6.7. The authors speculated that increased adsorption on soil colloids in acidic soils (resulting in lower bioavailability of the compound) caused decreased microbial degradation at the lower pH values. Greater movement of metribuzin was noted on soil thin-layer plates as pH increased, indicating lower soil adsorption at higher soil pH. (The authors did not provide adsorption coefficients.) Ladlie et al. (1976a) suggested that the expected optimal pH for maximum adsorption of metribuzin to soil colloids should be between pH 4.0 and 5.0. The influence of pH on adsorptive processes has been disputed by several investigators (e.g., Ballerstedt and Banks 1982).

Ladlie et al. (1976b, 1976c) demonstrated during field studies that the half-life of metribuzin was lessened as soil pH increased. Conversely, the half-life was greater with depth in the soil (but see Kempson-Jones and Hance 1979). The increased

leaching, mobility, and rate of dissipation at higher soil pH were attributed to decreased adsorption. The phytotoxicity of metribuzin also appeared to be positively correlated with soil pH. This latter process has also been reported by Warnes et al. (1977). In this latter study, injury to sugarbeet crops on a silty clay loam soil in Minnesota due to carry-over of metribuzin residues from the previous year was recorded. Sugarbeet yield was reduced by 83%. Plant injury (calculated using an index of injury) increased with soil pH. Two years after the metribuzin was applied, phytotoxicity to sugarbeets was not observed.

Scott and Paetzold (1978) investigated the effects of soil moisture and temperature on the diffusion of metribuzin in a silt loam soil under laboratory conditions. Metribuzin was found to diffuse in both liquid and vapour phases. Diffusion increased with increasing soil water content and soil temperature. The diffusion coefficient was lowest ($0.16 \pm 0.08 \times 10^6$ $cm^2 \cdot sec^{-1}$) at a temperature of 5°C and a soil water content of 0.05 $g \cdot g^{-1}$, and increased in a relatively linear manner with increasing temperature and moisture content (maximum of $1.17 \pm 0.36 \times 10^6$ $cm^2 \cdot sec^{-1}$ at 35°C and 0.10 $g \cdot g^{-1}$ soil moisture). The authors concluded that adsorption by soil colloids lowered the diffusion coefficient. Metribuzin is moderately adsorbed on soils with high clay and/or organic content matter and is readily leached in sandy soils low in organic matter (U.S. EPA 1988). Harper (1988) found that in silty clay loam surface and subsurface soils, clay was the best predictor of metribuzin adsorption and that pH, organic matter, and sand content were not related to adsorption.

Peek and Appleby (1989) recently studied the influence of soil properties on metribuzin phytotoxicity, adsorption, and mobility. They found that metribuzin was more mobile in coarse soils and that the adsorption coefficients for various soils were negatively correlated with the mobility. The only soil property significantly correlated with herbicide behaviour was sand content, with mobility being increased and phytotoxicity being diminished by increased sand content. Adsorption K_d values were not related to soil properties in any soil, although adsorption tended to increase as sand content and pH decreased. Metribuzin was more phytotoxic in high pH soils, possibly due to increased leaching losses in the more alkaline soils. The authors found a negative correlation ($r = -0.59$) between soil organic matter content and mobility, but this relationship was not significant. Other investigators have reported increased adsorption with increased organic matter content (Peter and Weber 1985; Savage 1976; Sharom and Stephenson 1976).

The sorption equilibria and relative mobility of metribuzin were evaluated in laboratory studies by Savage (1976) using 16 soils from the lower alluvial flood plain of the Mississippi River. Sorption and mobility were significantly correlated with clay, organic matter, and water content. The addition of clay colloid appeared to decrease the adsorbing capacity of the organic fraction. For example, the addition of clay (to 40%) to soils with high organic matter levels (6%) resulted in an approximate three-fold decrease in relative adsorption when compared to soil without the clay amendments. Thus there appeared to be competition between metribuzin and clay for sites that would be available for metribuzin adsorption.

Peter and Weber (1985) found that with higher organic matter and clay content, there was increased adsorption, and higher treatment rates were required to achieve the same level of weed control. In an accompanying soil column leachate test, they found that in an anaerobic sandy loam soil maintained in a saturated state (2.2 cm of water per day for 24 d), about 80% of the applied radioactively labelled metribuzin was recovered in the leachate. No metabolites of metribuzin were detected in either the soil or leachate, which suggested limited microbial degradation under these conditions. (The U.S. EPA [1987] reported that ^{14}C-metribuzin residues degraded slowly in silty clay soil under anaerobic conditions with a half-life of more than 70 d. No other reports of anaerobic degradation were found in the literature.)

Other leaching column experiments on metribuzin were carried out by Jarczyk (1972). Metribuzin, applied at a field rate of 1.05 $kg \cdot ha^{-1}$ on the soil surface, was leached through a soil column with 200 mm of water over 48 h. No measurements for the presence of metribuzin metabolites were made. In one soil tested (0.75% organic carbon, 12% clay, 5.3% silt, pH 5.6), 1.4% of the applied herbicide was recovered in the leachate from the 30-cm columns after continuous application of the water over 48 h. In a second soil (3.2% organic carbon, 9.8% clay, 10.3% silt, pH 5.2), no metribuzin was detected in the leachate after the same time period. In these first two soils, 50% of the applied metribuzin remained in the 15- to 25-cm soil layer. In a third soil (1.05% organic carbon, 18.2% clay, 12.2% silt, pH 5.7), the leachate contained 24% of the applied metribuzin. In this latter soil, the application of 50 mm of water over 5 d resulted in no detectable residues of metribuzin (detection limit

0.05 $mg \cdot L^{-1}$) in the leachate collected, while 59% of the herbicide was in the top 0- to 5-cm layer. The authors stated that the conditions for the third leaching experiment most closely resembled actual field conditions. They concluded that metribuzin will not penetrate deeply into the soil profile since the active ingredients are retained by adsorption on soil particles in the upper soil layers. Thus, there is little risk of metribuzin appearing in ground water.

Smith and Willis (1985) conducted a soil column leaching study to characterize the movement of metribuzin in soil as affected by the addition of anhydrous ammonia fertilizer. The sand content of the silt loam soil (23% sand, 67% silt, 10% clay, 0.31% organic matter) was raised with builder's sand to 50% to facilitate water movement, the soil column was brought to 21.0% moisture content by weight, and metribuzin was incorporated at 5 $\mu g \cdot g^{-1}$, along with 5 $\mu g \cdot g^{-1}$ of trifluralin, to the 2.5- to 10-cm soil zone. The columns (10.2 cm i.d.) were leached with 3 pore volumes (1500 mL each) of water at 20 $mL \cdot h^{-1}$. The mobility of metribuzin in this sandy soil was high. Metribuzin was recovered in all soil layers up to a depth of 37.5 cm, where the leachate was collected. Total metribuzin recovery in the leachates ranged from 54% to 74% of that applied. The first leachate, recovered after 1500 mL of water had passed through the column, typically contained over 40% of the metribuzin applied. Mobility of metribuzin appeared to be unaffected by anhydrous ammonia addition, but total metribuzin recoveries (column plus leachates) decreased with increasing anhydrous ammonia application. The authors suggest that this may be attributed to the alkali-solubilized humic substances promoting decomposition of the herbicide or the increased microbial degradation of metribuzin at higher pH levels.

Metribuzin was very mobile in a sandy loam and Louisiana silt loam; after 30.5-cm soil columns were leached with 51 cm of water, over 91% of the radioactivity was found in the leachate (U.S. EPA 1987). In an Indiana silt loam and a New York muck, over 89% of the applied radioactivity remained in the top 3 cm of the soil columns; no radioactivity was detected in the column leachates. In the Regina heavy clay studied in the field experiment conducted in Saskatchewan by Smith and Walker (1989), metribuzin did not leach below 10 cm during the 106-d growing season.

The results of a number of persistence studies undertaken with metribuzin in laboratory incubation or leaching column experiments, or in field trials, are summarized in Appendix B. The data indicate that the half-life of metribuzin as measured under field conditions is approximately 40 d. Scott (1975) reported a much faster rate of disappearance: a half-life of 7.88 d on a field plot. In these experiments, however, an abnormally high rate of application was used and maximum leaching conditions were maintained. (The metribuzin was applied with 3200 L of water to completely water-saturated, diked field plots, which were then covered with 8 cm of water.) As the pond half-life for metribuzin is about 6.5 d (see below), this result would appear to be more indicative of a pond half-life than a soil half-life.

Bouchard et al. (1982) reported that under winter conditions in Arkansas, the half-life of metribuzin (28 weeks) is greater than that measured for summer conditions (2.6 weeks). The temperature dependence of the rate of metribuzin degradation was also noted in laboratory incubation studies by Conn and Cameron (1988) and Hyzak and Zimdahl (1974). In the latter study, half-life values decreased from 377 d to 16 d with a temperature increase from 5°C to 35°C.

Metribuzin residues in runoff water were monitored from a winter wheat plot in Washington following fall surface applications (Brown et al. 1985). There was little movement or degradation of the herbicide while the ground was frozen. The concentrations of metribuzin in runoff water seen in this study and in an earlier one (Brown et al. 1984) reflected the fact that little degradation occurred while the soil was frozen.

The soil persistence of metribuzin in subarctic interior Alaska was examined by Conn and Cameron (1988). They studied the temporal pattern of metribuzin degradation in cold, silt loam soils after a single spring application of 0.3, 0.6, or 1.3 $kg \cdot ha^{-1}$. The rate of metribuzin degradation over the first, comparatively warm, growing season was similar to that reported for more southerly locations in Canada and the United States, but there was no degradation of metribuzin over the winter when the soil was frozen. The loss of metribuzin with time was (in percentages of the initial application remaining) 83% immediately post-application, 12% at the end of the first growing season, 9% after the second growing season, and 2% after the third growing season. The authors speculated that the initial rapid degradation of metribuzin in Alaska occurred because the herbicide was applied to vegetation and to the soil surface when the growing season temperatures were conducive to microbial degradation.

Of particular interest with respect to metribuzin degradation is the work of Webster and Reimer (1976a), who investigated the loss of this herbicide at −37°C ± 5°C in soil samples stored pending analysis. They estimated a half-life in a fine sandy loam containing 0.5 $\mu g \cdot g^{-1}$ of metribuzin to be 282 days at −37°C. Thus storage losses may be the cause of some of the variations in reported half-life values seen in the literature. Hatzios and Penner (1988) stated that results of experiments should be corrected for residue losses in samples stored for any length of time. Brown et al. (1984), however, claim that metribuzin can be stored in water for up to 300 days at −15°C.

Water and Sediment

Data on the aquatic fate of metribuzin are scarce (Table 3). Half-life estimates suggest a short aquatic persistence for this compound. Shaw and Flint (1971) reported a metribuzin half-life in pond water of 6.5 d at pH 7 (no further details were provided). In pond studies, the half-lives of technical grade metribuzin and the 70% wettable powder formulation were 2.5 and 6.5 d respectively (U.S. EPA unpub. data). Again, no further details were provided. Bioaccumulation is likely negligible as suggested by the low octanol/water partition coefficient for the compound (Table 1). Volatilization to the atmosphere would not be a major fate process (low vapour pressure, Table 1) for metribuzin in water (Muir 1990).

Little information was found on the adsorption of metribuzin to aquatic sediment. Frank et al. (1979) found no metribuzin in 45 suspended solids samples collected from 12 streams flowing into the Great Lakes from Ontario between 1974 and 1976 (detection limit 0.05 $\mu g \cdot g^{-1}$).

Data on the adsorption of this herbicide to walls of containers used in bioassays have been published. This process is relevant to residue analysis as it may result in a reduction of the effective concentration of the compound in bioassays. Sharom and Solomon (1981) found that 0.22% ± 0.3% of the initial concentration of metribuzin (1348 $\mu g \cdot L^{-1}$) was adsorbed on glass, but 45.63% ± 7% was adsorbed to polyvinyl chloride containers. Atrazine exhibited similar adsorption behaviour on these two surfaces (Sharom and Solomon 1981). Brown et al. (1984), however, stated that their "data indicate that neither metribuzin nor DADK and bromoxynil are adsorbed significantly by glass or high-density polyethylene from solutions containing up to 300 [$\mu g \cdot L^{-1}$] of the compounds" (Brown et al. 1984, pp. 199-200).

RATIONALE

Raw Water for Drinking Water Supply

Guideline

In 1989, Health and Welfare Canada published a MAC (maximum acceptable concentration) for metribuzin of 80 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1989). This value came from an allowable daily intake (ADI) of 0.0083 $mg \cdot kg^{-1}$ body weight based on 2-year feeding studies with dogs (Health and Welfare Canada, unpub. data). At higher dosages during these studies, the effects observed included reduced body weight gain and food consumption, increased thyroid, spleen, and kidney weight relative to body weight, and an increase in the incidence and severity of mucopolysaccharide droplets in the lobular periphery of the liver (K. Hughes, 1989, Health and Welfare Canada, pers. com.).

The U.S. EPA's lifetime health advisory for metribuzin is 175 $\mu g \cdot L^{-1}$ (U.S. EPA 1987). According to Wnuk et al. (1987), this health advisory reflects concentrations based upon noncarcinogenic, chronic toxicity which "appears to be without an appreciable risk of deleterious effects over a lifetime of exposure" (for a known or probable human carcinogen, the lifetime health advisory level is zero). The U.S. EPA (1987) listed their 1-d health advisory for a 10-kg child as 4.5 $mg \cdot L^{-1}$ (4500 $\mu g \cdot L^{-1}$); the 10-d advisory for the child was also 4.5 $mg \cdot L^{-1}$; the longer term (approximately 7-year) health advisory was 250 $\mu g \cdot L^{-1}$ for children and 875 $\mu g \cdot L^{-1}$ for adults. The U.S. EPA (1987) also reported a "threshold limit value-time-weighted average" developed by the American Conference of Governmental Industrial Hygienists for repeated metribuzin inhalation of 5 $mg \cdot m^{-3}$, based on animal studies and a safety factor of 5. The shorter term health advisories are based on intake of contaminated drinking water only and do not consider intake from other sources (e.g., residues in or on food).

Concentrations in Drinking Water

Metribuzin contamination is rare in Canadian drinking water supplies. The Ontario Ministry of the Environment (OMOE) carried out extensive surveys of municipal waterworks and private wells in 1985 and 1986 (OMOE 1987a, 1987b). Analyses for metribuzin were conducted in 1985 at eight municipal waterworks on a total of 121 raw water samples and 111 treated water samples. Two positive results were

recorded in raw water; metribuzin concentrations of 0.8 and 2.4 $\mu g \cdot L^{-1}$ were detected in the Sydenham River at Dresden (2 of the 54 samples from this source). No metribuzin was detected in the treated water samples from any site. Of the 351 wells sampled in 1985 (1881 water samples), metribuzin was found in 21 samples. The maximum reported concentration in any well was 300 $\mu g \cdot L^{-1}$, but the majority of the positive samples (18 of 21) were below 12 $\mu g \cdot L^{-1}$ (OMOE 1987a). The authors did not speculate on the source of the heavy metribuzin loading to the single contaminated well, but the fact that this well was also heavily contaminated with other pesticides would suggest that it had been subjected to a spill or pesticide mishandling. The authors emphasized that their study included wells that were not selected at random, but were chosen to represent private wells that would be susceptible to pesticide contamination (e.g., shallow dug wells and sandpoints in sandy soils in agricultural areas).

In the subsequent 1986 survey (OMOE 1987b), strict criteria for sample site selection were imposed to preclude sampling any wells that may have been subjected to the runoff contamination observed in the 1985 survey. A total of 37 domestic wells and 5 municipal ground-water supply wells in areas of intense corn and soybean production in southern Ontario were sampled. No metribuzin was detected (detection limit 0.1 $\mu g \cdot L^{-1}$). Of the 418 raw surface water samples taken at 25 different municipal waterworks, metribuzin was found at three waterworks: Alvinston and Dresden on the Sydenham River and Mitchell's Bay on Lake St. Clair. Each location had only one positive result at trace levels or above: 0.100, 1.700, and <0.080 $\mu g \cdot L^{-1}$, respectively. Metribuzin was not detected in any of the 150 treated water samples collected. The following year (1987), no metribuzin was detected in the surface water samples collected (Frank et al. 1990).

Removal by Water Treatment Operations

Conventional water treatment processes (i.e., chlorination) are not completely effective in removing metribuzin from contaminated water (Miltner et al. 1988; OMOE 1987a, 1987b; Wnuk et al. 1987; Frank et al. 1990). Powdered activated carbon (PAC) or granular activated carbon, if added in sufficiently high doses (40–50 $mg \cdot L^{-1}$ for PAC [OMOE 1987b], may be effective in reducing triazine concentrations in finished water (OMOE 1987a, 1987b; U.S. EPA 1987; Frank et al. 1990). Conventional water treatment with coagulation and sedimentation with alum ($ALSO_4 + KSO_4$) may remove more than 50% of the metribuzin from raw water (U.S. EPA 1987). The U.S. EPA (1987) concluded that for the removal of metribuzin from water, the selection of the appropriate technology requires a case-by-case evaluation and an assessment of the economics involved.

Freshwater Aquatic Life

Bioaccumulation

Metribuzin does not appear to bioaccumulate in aquatic organisms. An unpublished report by the U.S. EPA indicated that metribuzin did not accumulate in bluegill sunfish that were held in water containing 1.0 $mg \cdot L^{-1}$ of the compound (no other details were provided). However, data on metribuzin residue levels in biota are limited. The compound has a low predicted bioaccumulation potential (log K_{ow} of 1.87, Table 1). Kenaga (1980) calculated bioconcentration factors of 11 and 4 based on the water solubility and soil adsorption coefficient of metribuzin, respectively. Roberts et al. (1979) reported that no metribuzin residues were detected in whole fish homogenate of brown bullheads (*Ictalurus nebulosus*), gizzard shad (*Dorosoma cepedianum*), and black crappie (*Pomoxis nigromaculatis*) collected in the Hillman Creek watershed in Ontario in 1974 even though metribuzin had been found in 4.4% of the water samples collected there between 1973 and 1975. No metribuzin was found in 37 fish muscle samples (detection limit 0.04 $mg \cdot kg^{-3}$) collected in New Brunswick (Bailey 1985).

Toxicity to Aquatic Organisms

Data regarding the toxicity of metribuzin to aquatic organisms are summarized in Appendix C. These data indicate that aquatic plants and algae are much more sensitive to the toxic effects of metribuzin than vertebrate species. Some of the data cited in Appendix C are from secondary sources (U.S. EPA 1988; Verschueren 1983) in which the toxicity testing methodology was not described. Toxicity data from these sources are provided for comparison, but were not used for guideline development. Richardson et al. (1979), for instance, investigated the effects of metribuzin on the green alga *Euglena gracilis*. They found a stimulation of oxygen uptake in *Euglena* cells exposed to metribuzin and concluded that the response may be due to an uncoupling of respiration in the cells. *Euglena* chlorophyll content was reduced 67% by a 96-h exposure to a metribuzin concentration of 0.43 $mg \cdot L^{-1}$, and 78% by a concentration of

107 $mg \cdot L^{-1}$. In addition, photosynthesis, as measured by oxygen evolution, was reduced by 50% or more by metribuzin concentrations in excess of 0.193 $mg \cdot L^{-1}$ and totally inhibited by 0.43 $mg \cdot L^{-1}$ after 100 minutes of exposure. After 96 h of exposure, however, this latter concentration resulted in only a 46% reduction in photosynthesis, suggesting that algal metabolism and detoxification of the metribuzin were occurring. Metribuzin did not have a long-term inhibitory effect on cell numbers at any concentration studied (0.107 $mg \cdot L^{-1}$ to 107.1 $mg \cdot L^{-1}$). Despite an initial decline in cell numbers, after 144 h of exposure, cell numbers in the metribuzin-treated cultures returned to control levels or levels above control. Removal of *Euglena* from the treated media to untreated fresh media resulted in increased chlorophyll concentrations to levels near or greater than that of controls after 144 h.

Growth responses of five species of soil and aquatic algae to analytical grade metribuzin and its 6-isopropyl and 6-cyclohexyl analogues were examined by Arvik et al. (1973). Several species of green algae (*Chlorella vulgaris*, *Chlorococcum* sp., and *Chlamydomonas* sp.) and the blue-green alga *Anabaena* sp. were exposed to 0.05, 0.1, 0.5, and 1.0 $mg \cdot L^{-1}$ of the herbicides in liquid nutrient. The blue-green alga *Schizothrix calcicola* was exposed to equivalent levels in soil culture. *Anabaena* sp. did not exhibit a decrease in growth after application of 0.05 $mg \cdot L^{-1}$ of the 6-cyclohexyl analogue. After addition of 0.05 $mg \cdot L^{-1}$ of metribuzin, *Chlorella vulgaris* and *Chlamydomonas* sp. did not grow (based on turbidimetric measurements) relative to controls. At 1.0 $mg \cdot L^{-1}$ of metribuzin and its analogues, none of the algae exhibited growth. The authors calculated a lowest-observed-effect concentration (LOEC) of 0.05 $mg \cdot L^{-1}$ for all species and the three herbicides based on a significant inhibition of growth ($p = 0.05$) as compared to controls.

The influence of metribuzin on a solution containing a mixed culture of bacteria was studied by Gadkari (1984, 1985). Concentrations of 50 and 100 $mg \cdot L^{-1}$ did not produce any retarding effect on ammonia oxidation by the bacteria (species not given). However, at both concentrations, a moderate increase in nitrite oxidation was noted. Gadkari (1987) also added metribuzin to culture vials containing the cyanobacteria *Anabaena cylindrica* and *Nostoc muscorum*. When *A. cylindrica* was treated with a metribuzin concentration of 10 $mg \cdot L^{-1}$ (70% ai) for 4 d, the chlorophyll was eliminated and the cells became colourless (making further growth impossible). *A. cylindrica* had a high degree of sensitivity to metribuzin and even at 10 $mg \cdot L^{-1}$, the photosynthetic activity was blocked immediately. After 28 d of incubation, *A. cylindrica* had not recovered from the inhibiting effect of the metribuzin. *N. muscorum*, on the other hand, was resistent to metribuzin, although the basis of this resistance was not reported.

With the blue-green alga *Anaciptis nidulans*, growth and photosynthesis of log-phase algae were completely inhibited by 1000 $\mu g \cdot L^{-1}$ technical metribuzin. Inhibition was 93.5% with 500 $\mu g \cdot L^{-1}$ and 25% with 100 $\mu g \cdot L^{-1}$. Concentrations of 10 and 1 $\mu g \cdot L^{-1}$ were not inhibitory (Eley et al. 1983).

The LOEC reported for duckweed (*Lemna perpusilla*) in a series of bioassays conducted by Forney and Davis (1981) was 10 $\mu g \cdot L^{-1}$. These researchers found a significant ($p < 0.05$) inhibition of growth (31%) and reproduction of *Lemna* with a metribuzin concentration of 10 $\mu g \cdot L^{-1}$. After 4 weeks of growth, the 10 $\mu g \cdot L^{-1}$ of metribuzin initially added to the assay containers was still able to inhibit duckweed growth (amount of inhibition not reported) when all remaining plants were removed and fresh plants added. When compared to the reported aquatic half-life of metribuzin (6.5 d) (Shaw and Flint 1971), the herbicide appeared quite persistent under the conditions of this experiment, but the authors do not comment on this discrepancy. (The concentration of metribuzin in the water at 10 d was not measured.) The authors noted, however, that duckweed is used as a sensitive organism for the bioassay of photosynthesis-inhibiting herbicides in water.

Metribuzin acute toxicity LC_{50} values for some freshwater copepods and fish have been reported (U.S. EPA 1988; Worthing and Walker 1987; Mayer and Ellersieck 1986). The U.S. EPA (1988) stated that metribuzin is "moderately toxic to freshwater fish and invertebrates" and slightly toxic to shrimp (U.S. EPA 1988, p. 532). The lowest 96-h LC_{50} value reported for fish was 42 $mg \cdot L^{-1}$ for the rainbow trout (*Salmo gairdneri*). A 48-h LC_{50} of 150 $mg \cdot L^{-1}$ was reported for a mixed culture of the copepods *Diaptomus mississippiensis* and *Eucyclops agilis* (Naqvi et al. 1981). All reported LC_{50} values were well over the concentration of this herbicide that might occur in the environment, except after a severe spill. Inhibition of aquatic plant growth by metribuzin occurs at lower concentrations than those affecting invertebrates and fish, which is consistent with the herbicidal properties of this compound (see Appendix C).

Guideline

Few data were found concerning the toxicity of metribuzin to aquatic organisms. The majority of the available literature deals with the environmental fate of the herbicide, particularly as it relates to agricultural applications and the potential for persistence of phytotoxic soil residues. Reported concentrations in surface runoff and subsurface drainage from agricultural fields are low, and resultant contamination levels in receiving streams are generally low or not detectable. Data on the aquatic fate of metribuzin are particularly sparse. Half-lives in water would be expected to be less than a month (a pond half-life of 6.5 d has been published [Shaw and Flint 1971]), however, residues in sediments may persist longer. No evidence was found to suggest that this herbicide accumulates to high levels in aquatic organisms.

Exposure of aquatic organisms by means of waterborne concentrations of metribuzin washed into agricultural watersheds would most likely be of short duration and associated with runoff events shortly after soil application. However, chronic exposure from contaminated sediment cannot be discounted. Based on the data for sublethal exposure of the monocotyledon *Lemna perpusilla* (Forney and Davis 1981), an interim guideline for metribuzin of 1.0 $\mu g \cdot L^{-1}$ for the protection of all freshwater aquatic life is recommended. This is based on the application of a safety factor of 0.1 (CCREM 1987) to the LOEC of 10 $\mu g \cdot L^{-1}$ obtained for *L. perpusilla*, the most sensitive aquatic plant tested. This guideline value is one-half of the metribuzin concentration that would cause a 1% inhibition in the growth of *L. perpusilla*, an effect that the authors suggest would probably be "neither biologically significant nor detectable in either the laboratory or the field" (Forney and Davis 1981, p. 682). However, because of the limited data regarding the effects of metribuzin on primary producers, as well as on other aquatic organisms, and because of the discrepancies in the data regarding aquatic persistence, this guideline is given interim status.

Metribuzin toxicity values for fish are above the guideline limit (Appendix C). Reported 96-h LC_{50} values for bluegill sunfish ranged from 80 $mg \cdot L^{-1}$ to >100 $mg \cdot L^{-1}$; for rainbow trout, from 42 to 76 $mg \cdot L^{-1}$; for harlequin fish, 140 $mg \cdot L^{-1}$; and for channel catfish, >100 $mg \cdot L^{-1}$ (Worthing and Walker 1987; Mayer and Ellersieck 1986).

Data Gaps

More information is needed on the residual levels of metribuzin that might occur in fish after aquatic contamination by the herbicide. No microcosm studies were found that studied that fate of metribuzin in an aquatic ecosystem, and little information is available concerning the aquatic fate of the compound.

Few data are available on the toxicity of metribuzin to lower trophic level organisms. Because of the mode of action of this herbicide, adverse impacts on the aquatic primary producer community cannot be ruled out. As these organisms are quite important in aquatic ecosystems, further investigations should be made into the toxicity of metribuzin to phytoplankton. Information is also lacking with respect to secondary or indirect impacts of low levels of metribuzin if primary production or dissolved oxygen regimes in aquatic systems are adversely affected.

In a static study (Forney and Davis 1981), the persistence of metribuzin phytotoxicity remained for 4 weeks. This would suggest a longer persistence than the reported pond half-life of 6.5 d (Shaw and Flint 1971) or the presence of toxic metabolites following the aquatic degradation of metribuzin. The aquatic persistence and degradation of metribuzin needs to be further studied to address this discrepancy.

Agricultural Uses

Livestock Watering

Toxicity to Livestock and Related Biota

A recommended guideline for metribuzin in water used for livestock watering is based on the toxicity of metribuzin to mammals and birds. The available data on laboratory species, including rodents and dogs, indicate that metribuzin exhibits low toxicity through oral, dermal, and inhalation routes of exposure. No cases of wildlife poisoning have been located in the literature nor evidence of accumulation of metribuzin in the tissues of mammalian species. Acute and chronic toxicity indices for metribuzin in animals are summarized in Table 4.

Acute and Chronic Toxicity—Tomaszewski et al. (1985, 1986) stated that the oral LD_{50} was 250 $mg \cdot kg^{-1}$ b.w. for guinea pigs. In their study, 40 guinea pigs received a dose of 82.5 $mg \cdot kg^{-1}$

metribuzin directly into the gastric lumen six times per week for 30 or 90 d. The animals tolerated the metribuzin intoxication up to the twentieth day of treatment after which there was a deterioration in their general health including loss of weight. After 90 d, the liver of treated animals was congested and exhibited degeneration and necrosis of individual cells; impairment of liver cells first appeared after 30 d of treatment. The authors concluded that metribuzin probably damages the plasma membranes of liver cells and inhibits liver carbohydrate and protein biosynthesis, which may lead to progressive immunodeficiency. Löser and Kimmerle (1972) noted that of the species they tested, guinea pigs were the most sensitive to metribuzin.

Bleeke et al. (1985) also noticed hepatotoxicity in mice treated with metribuzin at intraperitoneal doses of 200 $mg \cdot kg^{-1}$ or above. Their LD_{50} values for male albino mice 24 h after a single intraperitoneal injection were 210 $mg \cdot kg^{-1}$ (95% confidence interval [C.I.] = 85–275 $mg \cdot kg^{-1}$) for metribuzin and 130 $mg \cdot kg^{-1}$ (C.I. = 95–160 $mg \cdot kg^{-1}$) for deaminated metribuzin. Bleeke et al. (1985) concluded that the toxicity of metribuzin is apparently due in part to metabolic activation of the compound to the electrophilic sulfoxide. These intermediate sulfoxides have high reactivity (Hatzios and Penner 1988). One other 24-h intraperitoneal metribuzin LD_{50} for mice has been reported as 247 $mg \cdot kg^{-1}$ b.w. (Löser and Kimmerle 1972).

The acute oral LD_{50} for metribuzin-treated mice has been reported to be between 698 and 711 $mg \cdot kg^{-1}$ b.w. (Löser and Kimmerle 1972). For rats, the acute oral LD_{50} ranged from 2200 to 2345 $mg \cdot kg^{-1}$ b.w. (Löser and Kimmerle 1972). Metribuzin fed to 10 white rats at 110 $mg \cdot kg^{-1}$ b.w. for 15 d caused congestion of the viscera and mild focal interstitial nephritis (Shihata et al. 1985). Acute

Table 4. Acute and Chronic Toxicity of Metribuzin to Mammals and Birds

Species	Route	Parameter	Concentration
Acute			
Rat	oral	LD_{50} ($mg \cdot kg^{-1}$ b.w.)	2200–2345 (males) 1090–1206 (females)
Mouse	oral	LD_{50} ($mg \cdot kg^{-1}$ b.w.)	698–711
Guinea pig	oral	LD_{50} ($mg \cdot kg^{-1}$ b.w.)	245–274
Rat	dermal	LD_{50} ($mg \cdot kg^{-1}$ b.w.)	>20 000
Quail	oral	LD_{50} ($mg \cdot kg^{-1}$ b.w.)	164–168
Rat	inhalation	NEL-3 weeks (6 $h \cdot d^{-1}$, 5d $\cdot week^{-1}$)	31 $mg \cdot m^{-3}$
Rat, mouse	inhalation	no mortalities, 4-h exposure	860–892 $mg \cdot m^{-3}$
Rat	inhalation	1 h LC_{50}	>20 $mg \cdot L^{-1}$
Chronic			
Rat	oral	NOEL-2 year ($mg \cdot kg^{-1}$ in diet)	100
Dog	oral	NOEL-2 year ($mg \cdot kg^{-1}$ in diet)	100
Rat	oral	NOEL-2 year ($mg \cdot kg^{-1} \cdot d^{-1}$ in diet)	20
Mouse	oral	NOEL-2 year ($mg \cdot kg^{-1} \cdot d^{-1}$ in diet)	120
Beagle dog	oral	NOEL-2 year ($mg \cdot kg^{-1} \cdot d^{-1}$ in diet)	2.5

Sources: U.S. EPA 1987; Worthing and Walker 1987; ACGIH 1986; Weed Science Society of America 1983.

oral toxicity LD_{50} values for metribuzin fed to cats and rabbits were above 500 $mg \cdot kg^{-1}$ b.w. (Löser and Kimmerle 1972).

The dermal and inhalation toxicities of metribuzin are low. Technical grade metribuzin and metribuzin 50% wettable powder taped to the abraded skin of rats for 24 h at an effective dose of 20 000 $mg \cdot kg^{-1}$ b.w. did not produce toxic symptoms (Weed Science Society of America 1983). Application of approximately 500 mg of metribuzin on cotton-wool pads to the inside skin of rabbits' ears and to the forearms of eight human volunteers for a period of 24 h caused no discernible skin injuries (Löser and Kimmerle 1972). The same authors reported that formulated metribuzin did not cause eye irritation in rabbits and did not sensitize the skin of treated rats. The U.S. EPA (1987) reported that metribuzin was a very slight irritant to rabbit eyes and skin. In inhalation studies, male and female rats survived dust treatments of 20 000 $\mu g \cdot L^{-1}$ formulated metribuzin (Weed Science Society of America 1983). Male rats exposed to 859 $mg \cdot m^{-3}$ of metribuzin for 20 h over 5 d survived the treatment, although the animals exhibited symptoms of toxicity (the actual symptoms were not reported) (Löser and Kimmerle 1972).

In 2-year feeding trials with rats and beagle dogs, the no-observed-effect levels (NOEL) were 20 $mg \cdot kg^{-1} \cdot d^{-1}$ b.w. and 2.5 $mg \cdot kg^{-1} \cdot d^{-1}$ respectively (U.S. EPA 1985). A NOEL for beagle dogs administered oral doses of technical metribuzin for 90 d was 12.5 $mg \cdot kg^{-1} \cdot d^{-1}$ (U.S. EPA 1987). Löser and Kimmerle (1972) found that rats that were fed 1500 $mg \cdot kg^{-1}$ in the feed for 3 months had significantly lower body weights than control animals. The animals had no haematological changes, but there were dose-related enlargements of their thyroids and livers and decreased visceral organ weights in the treatment group. At 50 $mg \cdot kg^{-1}$ in the feed (7.5 $mg \cdot kg^{-1} \cdot d^{-1}$), the female rats developed enlarged livers. Further 3-month feeding experiments with metribuzin concentrations of 60 $mg \cdot kg^{-1}$ in the feed revealed no changes in the rats, which ingested an average of 0.81 mg of metribuzin per animal per day. Metribuzin fed to dogs for 3 months in dietary concentrations of 50, 150, and 500 $mg \cdot kg^{-1}$ caused no discernible adverse effects in any of the animals (Löser and Kimmerle 1972).

The acute oral LD_{50} for hens was >1000 $mg \cdot kg^{-1}$ b.w. (Löser and Kimmerle 1972), and for bobwhite quail, 164–168 $mg \cdot kg^{-1}$ b.w. (Worthing and Walker 1987). Hatzios and Penner (1988) noted that oral LD_{50} values ranging from 500 to 1000 $mg \cdot kg^{-1}$ have been reported for several bird species, including mallard ducks, canaries, red-winged blackbirds, brownhead cowbirds, and house sparrows.

Carcinogenicity, Teratogenicity, and Genotoxicity—The U.S. EPA (1987) summarized the results of teratology studies with metribuzin. In a three-generation study, technical grade metribuzin fed to rats during mating, gestation, and lactation did not have any effects on fertility, lactation, and pup development at doses up to 15 $mg \cdot kg^{-1}$ b.w. $\cdot d^{-1}$. No maternal or fetal toxicity was observed when pregnant rabbits were administered oral doses of metribuzin at of 45 $mg \cdot kg^{-1} \cdot d^{-1}$ or less. No maternal toxicity, embryotoxicity, or teratogenic effects were seen following oral administration of metribuzin to rats given doses of up to 100 $mg \cdot kg^{-1}$ b.w. $\cdot d^{-1}$ (U.S. EPA 1987).

Wnuk et al. (1987, p. 33) summarized U.S. EPA toxicity data for metribuzin that were used to determine acceptable daily intake levels. Assuming the data concern doses of milligrams per kilograms of body weight, for metribuzin, the rabbit teratology NOEL was 15 $mg \cdot kg^{-1}$; the same NOEL for rats was 100 $mg \cdot kg^{-1}$. A 2-year dog-feeding NOEL was 100 $mg \cdot kg^{-1}$; for rats, 300 $mg \cdot kg^{-1}$. A 2-year mouse oncogenicity study was negative at 3200 $mg \cdot kg^{-1}$, and a three-generation reproduction test had a NOEL of 300 $mg \cdot kg^{-1}$.

Metribuzin was not able to induce a bacterial regulatory network affected by DNA damage on assays with *E. coli* conducted by Xu and Schurr (1990) and was labelled a negative genotoxic compound.

Guideline

Because of a lack of adequate subacute and chronic toxicology data for livestock consuming metribuzin in their water, it is difficult to develop a water quality guideline for livestock watering. An unpublished U.S. EPA study has reported that dairy cattle fed 10 $mg \cdot kg^{-1}$ metribuzin in their diet for 30 d had no detectable residues (detection limit 0.01 $mg \cdot kg^{-1}$) in their milk, but beef cattle on the same diet for 30 d had residues of 1.0 $mg \cdot kg^{-1}$ in the liver and 0.17 $mg \cdot kg^{-1}$ in the kidneys. Hens fed 15 $mg \cdot kg^{-1}$ in their diet for 30 d had 0.06 $mg \cdot kg^{-1}$ in their fat and muscle, 0.25 $mg \cdot kg^{-1}$ in their gizzards, and 0.04 $mg \cdot kg^{-1}$ in their eggs. In these studies, however, the metribuzin intake was not by

means of drinking water. Therefore, in the absence of sufficient information, the CCREM (1987) procedure of adopting the guideline value for human drinking water supplies is followed to develop an interim Canadian water quality guideline for livestock water. This would result in a recommended limit of 80 $\mu g \cdot L^{-1}$ of metribuzin in water provided for livestock watering.

Irrigation

Little information is available regarding the acceptable concentration of metribuzin in irrigation water. The U.S. EPA (1988) imposed a rotational crop restriction ground-water advisory for metribuzin to protect sensitive plants. The U.S. EPA also lists "current tolerance standards" for metribuzin ranging from 0.01 to 7 $mg \cdot L^{-1}$ depending on whether the registration is for food, animal feed, or commodity. (The food tolerance standard is generally 3 $mg \cdot L^{-1}$.) The two existing water quality guidelines for triazine herbicides in irrigation waters are 0.5 $\mu g \cdot L^{-1}$ (OMOE 1984) and 10 $\mu g \cdot L^{-1}$ (U.S. EPA 1977). The OMOE (1984) limit is based on the ability of the triazine herbicides to injure seedling crops at this concentration. The specific mode of action of the triazine herbicides (inhibition of photosynthesis) prompted the U.S. EPA (1977) guideline.

For nontarget plant species, Ratsch et al. (1986) determined metribuzin sensitivity with a plant life-cycle bioassay using the small herbaceous test species *Arabidopsis thaliana*. Metribuzin significantly suppressed vegetative and mature seed weights. Chemical sensitivity, as determined by the concentrations that suppressed growth by 50%, was as low as 7.0 $\mu g \cdot L^{-1}$. The "effect threshold concentration" for metribuzin was 5.0 $\mu g \cdot L^{-1}$. Harrison et al. (1987) found that a metribuzin soil concentration of 300 $\mu g \cdot kg^{-1}$ severely injured susceptible sweet potato clones.

Guideline

The OMOE (1984) noted that concentrations of triazine herbicides (including metribuzin) as low as 0.5 $\mu g \cdot L^{-1}$ may injure seedling crops. Several investigations with metribuzin, however, have shown that the tolerance of crop species to metribuzin may be higher (Frank and Beste 1983; Gawronski 1983; Chappell and Link 1977; da Silva and Warren 1976). For instance, some tobacco plants can survive an irrigation treatment of 1.5 $g \cdot L^{-1}$ (Chappel and Link 1977). Although there appear to be insufficient data with which to settle this discrepancy, an interim Canadian water quality guideline for metribuzin in irrigation water of 0.5 $\mu g \cdot L^{-1}$ may be recommended by choosing the lowest value at which toxic effects may occur (OMOE 1984). It is appropriate to choose a low value for this guideline, as with metribuzin, an inhibitor of photosynthesis, this may be the most critical water use.

Recreational Water Quality and Aesthetics

Guideline

There is no recommended limit for metribuzin in recreational waters. No evidence was found in the literature that would suggest that the presence of this herbicide in water would result in any aesthetic impairment at concentrations below those that would be deleterious for other water uses.

Industrial Water Supplies

Guideline

There is no recommended limit for metribuzin in industrial water supplies.

SUMMARY

Following an extensive evaluation of the published literature on the pesticide metribuzin, Canadian water quality guidelines were derived (Table 5). The background information on metribuzin in terms of uses and production, occurrence in the aquatic environment, and persistence and degradation was reviewed.

Table 5. Recommended Water Quality Guidelines for Metribuzin

Uses	Guidelines
Raw water for drinking water supply	80 $\mu g \cdot L^{-1}$ (MAC)*
Freshwater aquatic life	1 $\mu g \cdot L^{-1}$ (interim)
Agricultural uses	
Livestock watering	80 $\mu g \cdot L^{-1}$ (interim)
Irrigation	0.5 $\mu g \cdot L^{-1}$ (interim)
Recreational water quality and aesthetics	No recommended guideline
Industrial water supplies	No recommended guideline

*Existing drinking water guideline (Health and Welfare Canada 1989).

The rationale employed for the development of the recommended guidelines was summarized.

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Appendix A
Environmental Concentrations of Metribuzin Residues in Water, Sediment, and Biota

Table A-1. Environmental Concentrations of Metribuzin Residues in Water, Sediment, and Biota

Sample	Location	Concentration mean	Range	Number of samples	Year(s)	Reference
Surface water	Hillman Creek drainage, southwestern Ontario, agricultural watershed	—	<0.1–22.0 $\mu g \cdot L^{-1}$	Detected in 16 of 360 samples (4.4%).	1973–1974	Roberts et al. 1979
Surface water	11 agricultural watersheds in southern Ontario	0.02 $\mu g \cdot L^{-1}$	ND*–1.4 $\mu g \cdot L^{-1}$	—	1975–1976	Frank et al. 1982
	11 agricultural watersheds in southern Ontario	0.02 $\mu g \cdot L^{-1}$	ND–1.2 $\mu g \cdot L^{-1}$	—	1976–1977	
Surface water	Mouths of 92 streams mostly in southern Ontario draining into Great Lakes	(only one stream, Ruscom River, had detectable residue at a level of 0.4 $\mu g \cdot L^{-1}$)	—	92	July 1977	Frank et al. 1979
Ground water	2 rural farm wells in southern Ontario, mineral soils	—	ND–42 $\mu g \cdot L^{-1}$ (detection limit 0.1 $\mu g \cdot L^{-1}$) Maximum concentration due to spill in dug well drilled to 33 m in clay soil. Disappearance with time: 25 Nov. 84 — 42 $\mu g \cdot L^{-1}$ 4 Apr. 85 — 2.0 $\mu g \cdot L^{-1}$ 9 July 85 — 1.9 $\mu g \cdot L^{-1}$ 13 Aug. 85 — 0.8 $\mu g \cdot L^{-1}$ 22 Aug. 85 — 1.6 $\mu g \cdot L^{-1}$	Detected in 1 of 91 farms surveyed, while 16 of 91 farms had used the herbicide.	1984	Frank, Ripley, et al. 1987
Surface water	2 agricultural watersheds in northwestern Ohio, Maumee River and Sandusky River	1.53 $\mu g \cdot L^{-1}$	ND–4.9 $\mu g \cdot L^{-1}$	Detected in 34 of 39 samples (87.2%).	1984	Miltner et al. 1988

* ND = not detected

Table A-1. Continued

Sample	Location	Concentration mean	Range	Number of samples	Year(s)	Reference
Surface water	Water samples from water treatment plant influent	0.89 $\mu g \cdot L^{-1}$	ND–3.5 $\mu g \cdot L^{-1}$	Detected on 11 of 17 sampling days.	1984	Miltner et al. 1988
Ground water	Rural farm wells in southern Ontario suspected of contamination	—	ND–187 $\mu g \cdot L^{-1}$ (detection limit 0.1 $\mu g \cdot L^{-1}$)	Detected in 2 of 160 wells suspected of contamination. Both positive results attributed to "spills."	1979–1984	Frank, Clegg, et al. 1987
			Well 1—pumped continuously for 20 d, intermittently thereafter (6-m dug well): Day 5 — 187 $\mu g \cdot L^{-1}$ Day 18 — 182 $\mu g \cdot L^{-1}$ Day 18 — 0.9 $\mu g \cdot L^{-1}$			
			Well 2—unspecified pumping schedule (5-m dug well): Day 95 — 59 $\mu g \cdot L^{-1}$ Day 136 — 17 $\mu g \cdot L^{-1}$ Day 230 — 13 $\mu g \cdot L^{-1}$ Day 291 — 2.7 $\mu g \cdot L^{-1}$			
Suspended solids	Mouths of 12 southern Ontario streams flowing into the Great Lakes	ND (<0.05 $\mu g \cdot g^{-1}$)	—	45	1974–1976	Frank et al. 1979
Fish (*Ictalurus nubulosus*, *Dorosoma cepedianum*, *Pomoxis nigromaculatis*)	Hillman Creek drainage, southwestern Ontario, agricultural watershed	ND (detection limit not given)	—	33	1974	Roberts et al. 1979

Table A-1. Continued

Sample	Location	Concentration mean	Range	Number of samples	Year(s)	Reference
Surface water	Public drinking water supplies from surface water sources in Iowa, sampled during spring runoff.	0.29 $\mu g \cdot L^{-1}$ in treated water 0.89 $\mu g \cdot L^{-1}$ in untreated water	0.14–0.45 $\mu g \cdot L^{-1}$	Detected in 4 of 33 treated water samples and 1 of 15 untreated samples.	1986	Wnuk et al. 1987
Surface water	Lake in an agricultural watershed along the Kansas-Nebraska border	0.33 $\mu g \cdot L^{-1}$	—	Detected in 1 of 7 samples.	1985	Arruda et al. 1988
Surface water	Southwestern Ontario, mouths of the Grand, Saugeen, and Thames rivers	1.6 $\mu g \cdot L^{-1}$, 1981 0.3 $\mu g \cdot L^{-1}$, 1982 1.1 $\mu g \cdot L^{-1}$, 1985	—	Detected in 6 of 440 samples.	1981–1985	Frank and Logan 1988

Appendix B

Summary of Metribuzin Persistence Studies in Soil

Table B-1. Summary of Metribuzin Persistence Studies in Soil

Location/soil type (% organic matter; pH; moisture content)	Application rate	Soil depths measured	Residues (days after treatment)	Results and comments	Reference
FIELD STUDIES					
Germany (Carbon — 2.1% Clay — 12.3% Silt — 17.6% pH — 7.0)	1.05 $kg \cdot ha^{-1}$	0–5 cm	0.05 $\mu g \cdot L^{-1}$ (90 days)	Uncropped fields, rainfall 427 mm. Half-life approximately 40 d.	Jarczyk 1972.
Colorado, U.S.A. Bay farm clay soil (Sand — 32% Silt — 27% Clay — 41% O.M. — 1.6% pH — 7.6%)	2.24 $kg \cdot ha^{-1}$	0–5 cm	—	Half-life = 43 days.	Hyzak and Zimdahl 1974.
	1.12 $kg \cdot ha^{-1}$	0–5 cm	—	Half-life = 44 days.	
Fayetteville, Arkansas Captina silt loam, under maximum leaching conditions (see text)	45.6 $kg \cdot ha^{-1}$	0–121 cm	—	Half-life = 7.88 days on plot with vegetation cover (lower rate attributed to lower surface temperature due to vegetation shading).	Scott 1975.
	45.6 $kg \cdot ha^{-1}$	0–121 cm	—	Half-life = 5.13 days on plot without vegetation cover. (Metribuzin detected to a depth of 61 cm, however, most concentrated in top 23 cm. Persistence greatly influenced by microbial degradation.)	
Ontario Guelph loam (Sand — 24.1% Silt — 53% Clay — 23% O.M. — 5.7% pH — 7.2)	0–1.2 $kg \cdot ha^{-1}$	0–8 cm	—	Phytotoxicity half-life approximately 3 months as measured in cucumber bioassay. Half-life values increased with increasing application rates. Leaching of phytotoxic residues to the 8–16 cm depth occurred after 3 weeks at 1.12 $kg \cdot ha^{-1}$.	Sharom and Stephenson 1976.

Table B-1. Continued

Location/soil type (% organic matter; pH; moisture content)	Application rate	Soil depths measured	Residues (days after treatment)	Results and comments	Reference
Wellesbourne, UK Sandy loam (Clay — 18% O.M. — 2% pH — 7)	2.0 $kg \cdot ha^{-1}$	0–7.5 cm	5% (128 d)	Half-life approximately 40 d.	Walker 1978.
Fayetteville, Arkansas Taloka silt loam (Sand — 23.4% Silt — 67.5% Clay — 9.1% O.M. — 1.1% pH — 5.2%)	0.3 $\mu g \cdot g^{-1}$ (initial concentration)	Sample buried at 10–20 cm depth	ND at end of summer from tests initiated in October or May	Half-life approximately 28 weeks in winter and 3 weeks in summer employing a buried bottle technique, which prevented leaching.	Bouchard et al. 1982.
England Fallow, coarse sandy loam (O.M. — 1.2% Clay — 70% pH — 7.0)	2.0 $kg \cdot ha^{-1}$	0–15 cm	89 ± 4.9% (3 d) 66 ± 4.7% (14 d) 52 ± 2.6% (27 d) 31 ± 2.1% (57 d) 21 ± 1.5% (83 d) 7 ± 0.7% (111 d)	Half-life approximately 4 weeks. Highest concentration of residues found at the 2–3 cm depth. Little leaching beyond 10 cm depth.	Nicholls et al. 1982.
Saskatchewan Regina heavy clay (O.M. — 4.2% Clay — 70% Silt — 25% Sand — 5%)	1.0 $kg \cdot ha^{-1}$	0–10 cm	71 ± 11% (8 d) 49 ± 3% (40 d) 40 ± 2% (64 d) 31 ± 2% (106 d)	Half-life approximately 60 d (dry conditions). No leaching below 10 cm.	Smith and Walker 1989.
Prince Edward Island Loam to fine sandy loam (pH — 5.4 to 6.2 O.M. — 2.2 to 2.6% Sand — 49.3 to 55.0% Silt — 30.0 to 36.9% Clay — 13.8 to 17.2%)	0.5, 1.0, and 1.5 $kg \cdot ha^{-1}$	0–10 cm	—	Half-life estimates averaged over rates applied: 39 days in 1977, 32 days in 1978, and 30 days in 1979.	Ivany et al. 1983.

Table B-1. Continued

Location/soil type (% organic matter; pH; moisture content)	Application rate	Soil depths measured	Residues (days after treatment)	Results and comments	Reference
East Lansing, Michigan Hillside sandy loam (O.M. — 1.5% Sand — 53% Silt — 22% Clay — 25%)	1.12 kg·ha^{-1}	0–5 cm 5–10 cm 10–20 cm	—	Soil collected from field plots 15 to 150 d after preemergence application in each of 2 years. Half-life (d) at pH 4.6/5.6/6.7: 21/20/18 34/26/19 62/46/37	Ladlie et al. 1976c.
Saskatchewan field plots Sandy loam	1 kg·ha^{-1}	0–5 cm	1979 <2% after 154 d 1980 <2% after 154 d 1981 <6% ± 1% after 154 d	During 1979 and 1980 no metribuzin leached to the 5–10 cm depth. In 1981 5% leached to this depth in the sandy and clay loam and 15% in the heavy clay soil.	Smith and Hayden 1982.
Heavy clay	1 kg·ha^{-1}	0–5 cm	1979 2% after 154 d 1980 11% ± 5% after 154 d 1981 18% ± 8% after 154 d		
Clay loam	1 kg·ha^{-1}	0–5 cm	1979 <2% after 154 d 1980 <15% ± 10% after 154 d 1981 <20% ± 1% after 154 d		
Delta Junction, Alaska Volkmer and Beales silt loam	0.3, 0.6, and 1.3 kg·ha^{-1}		Percent metribuzin remaining: 83% after 1 d 12% after 89 d 13% after 311 d 9% after 392 d 9% after 692 d 2% after 1057 d	Little degradation or loss of metribuzin occurs over the winter months when the soil is frozen; growing season degradation rate equals that seen in southern Canada.	Conn and Cameron 1988.

Table B-1. Continued

Location/soil type (% organic matter; pH; moisture content)	Application rate	Soil depths measured	Residues (days after treatment)	Results and comments	Reference
GREENHOUSE EXPERIMENTS					
4 Puerto Rican soils (Sand — 33.4%–46.4% Silt — 18%–31% Clay — 27.6%–40.6% Organics — 2.7%–3.6% pH — 6.6–7.4)	2 $\mu g \cdot g^{-1}$	—	0.5%–5.0% (45 d)	Reference sparse on detail.	Vega et al. 1973.
Sharkey clay soil (Sand — 4% Clay — 71% O.M. — 4.2% pH — 5.5 Moisture content— 0.33 bar)	1.0 $\mu g \cdot g^{-1}$ (initial concentration)	0–10 cm	0.04 $\mu g \cdot g^{-1}$ (180 d)	Half-life = 17 days under greenhouse conditions and temperature range 23°C–38°C.	Savage 1977.
Bosket sandy loam (Sand — 22% Clay — 26% O.M. — 1.3% pH — 6.8 Moisture content— 0.33 bar)	1.0 $\mu g \cdot g^{-1}$ (initial concentration)	0–10 cm	0.06 $\mu g \cdot g^{-1}$ (180 d)	Half-life = 25 days under greenhouse conditions and temperature range 23°C–38°C	
LABORATORY STUDIES					
San Luis sandy Loam (Sand — 69% Silt — 11% Clay — 20% O.M. — 1.6% pH — 7.6 moisture—field capacity)	10 $\mu g \cdot g^{-1}$ (initial concentration)	—	—	Laboratory incubation study; half-life = 377 d at 5°C = 46 d at 20°C = 16 d at 35°C	Hyzak and Zimdahl 1974.
Sassafras sandy loam (Sand — 56% Silt — 32% Clay — 12% O.M. — 3.04% pH — 5.7% moisture = 60% of field capacity)	10 $\mu g \cdot g^{-1}$	—	55% (6 d) 10% (42 d)	Soil incubation study at 28°C in the dark.	Lay and Ilnicki 1974.

Table B-1. Continued

Location/soil type (% organic matter; pH; moisture content)	Application rate	Soil depths measured	Residues (days after treatment)	Results and comments	Reference
Regina heavy clay (Sand — 5% Silt — 25% Clay — 70% O.M. — 4.2% pH — 7.7)	2.0 $\mu g \cdot g^{-1}$	—		Laboratory incubation study; half-life at 34% moisture (85% field capacity) = 22 d at 30°C = 32 d at 25°C = 34 d at 20°C = 62 d at 15°C = 94 d at 10°C = 193 d at 5°C half-life at 25°C = 28 d at 40% moisture = 32 d at 34% moisture = 63 d at 26% moisture = 112 d at 20% moisture = >300 d at 8% moisture	Smith and Walker 1989.
Manitoba (4 Manitoba soils, all sterilized)	initial concentration			Laboratory incubation study at 15°C. Half-life values as follows for sterilized conditions:	Webster et al. 1978.
— Red River clay (Clay — 50.3% O.M. — 8.6%)	1.8 $\mu g \cdot g^{-1}$ 18 $\mu g \cdot g^{-1}$	—	—	101 d 108 d	
— Clay loam (Clay — 30.5% O.M. — 4.7%)	1.8 $\mu g \cdot g^{-1}$ 18 $\mu g \cdot g^{-1}$	—	—	348 d 423 d	
— Very fine sandy loam (Clay — 11.3% O.M. — 3.5%)	1.8 $\mu g \cdot g^{-1}$ 18 $\mu g \cdot g^{-1}$	—	—	93 d 187 d	
— Sandy loam (Clay — 10.5% O.M. — 2.4%)	1.8 $\mu g \cdot g^{-1}$ 18 $\mu g \cdot g^{-1}$	—	—	115 d 124 d	

Table B-1. Continued

Location/soil type (% organic matter; pH; moisture content)	Application rate	Soil depths measured	Residues (days after treatment)	Results and comments	Reference
Idaho Portneuf silt loam (pH — 6.8 O.M. — 3%)	2.0 $\mu g \cdot g^{-1}$ (initial concentration)	—	—	Laboratory incubation study. Half-life = 21 d at 25°C.	Pettygrove and Naylor 1985.
	10 $\mu g \cdot g^{-1}$ (initial concentration)	—	—	Laboratory incubation study. Half-life = 29 d at 25°C.	
Ontario Embro silt loam (Sand — 10.6% Silt — 65.8% Clay — 23.6% O.M. — 7.0% pH — 6.4)	—	—	—	Laboratory incubation study. Half-life = 2.5 months at 27°C.	Sharom and Stephenson 1976.
Ontario Bradford muck (O.M. — 62.8% pH — 5.9)	—	—	—	Laboratory incubation study. Half-life = 4 months at 27°C.	Sharom and Stephenson 1976.
Silt loam soil (O.M. — 0.8% pH — 4.9–6.9, adjusted by lime)	0–1 $kg \cdot ha^{-1}$	—	—	Phytotoxicity half-life at 35°C = 8 days as measured by intact-plant chlorophyll fluorescence bioassay techniques. Soil pH had no significant influence on activity or persistence.	Shaw et al. 1986.
Mississippi, U.S.A. Mississippi delta soil Silty clay loam incubated in dark	1.0 $mg \cdot kg^{-1}$	0–10 cm 35–80 cm 125–150 cm	—	Of initial application percentage remaining after 91 d: 4% 15.8% 20.4%	Moorman and Harper 1989.

Table B-1. Continued

Location/soil type (% organic matter; pH; moisture content)	Application rate	Soil depths measured	Residues (days after treatment)	Results and comments	Reference
SOIL COLUMN LEACHING TESTS					
Loamy sand (pH — 6.0 Clay — 4.0% O.M. — 1.3%)	2.14 $\mu g \cdot g^{-1}$	0–100 cm	31% recovered in column, 54% in effluent, after 8 wetting events.	In these experiments water was added to 1-m columns in 3-cm units called "wetting events." Wetting schedule included 1 to 128 wetting events.	LaFleur 1980a.
Sandy loam (pH — 6.1 Clay — 11% O.M. — 2.0%)	2.14 $\mu g \cdot g^{-1}$	0–100 cm	69% recovered in column, 14% in effluent, after 8 wetting events.		

Appendix C
Acute Toxicity of Metribuzin to Aquatic Organisms

Table C-1. Acute Toxicity of Metribuzin to Aquatic Organisms

Species	Test conditions	Temp. (°C)	pH	Hardness (mg $CaCO_3$/L)	Formulation (% active)	LC_{50}/EC_{50} (mg·L^{-1})	Reference
Copepods (freshwater) (91% *Diaptomus mississippiensis*; 9% *Eucyclops agilis*)	static, aerated, unmeasured	18°C–21°C	7.0–6.4	—	—	24-h LC_{50} = 205 48-h LC_{50} = 150	Naqvi et al. 1981.
Daphnia magna first instar	static	18	7.4	40	90	48-h EC_{50} > 100	Mayer and Ellersieck 1986.
Fish (freshwater) rainbow trout (*Salmo gairdneri*)	static	12	7.3	40	90	96-h LC_{50} = 76 96-h LC_{50} = 42 (confidence interval = 33 to 54)	Worthing and Walker 1987. Mayer and Ellersieck 1986.
Fish (freshwater) bluegill sunfish (*Lepomis macrochirus*)	—	—	—	—	—	96-h LC_{50} = 76	U.S. EPA 1988.
Fish (freshwater) harlequin fish (*Resbora heteromorpha*)	flow-through unmeasured	20°C	8.1	20 mg·L^{-1}	70%	96-h LC_{50} = 140	Tooby et al. 1975.
Fish (freshwater) channel catfish (*Ictalurus punctatus*)	static, 0.22 g fish static, 0.92 g fish	22 22	7.4 7.5	40 42	90 90	96-h LC_{50} < 100 96-h LC_{50} > 100	Mayer and Ellersieck 1986.
Aquatic plants Egeria (*Egeria densa*) Elodea (*Elodea canadensis*)	static, unmeasured (3–4 week exposures). Growth inhibition IC_{50} and IC_1 from linear regression analysis. LOEC represents concentration where inhibition was significantly different from control value ($P = 0.05$); the authors have reservations about their linear regression analysis.	20°C–30°C	—	—	—	IC_{50} = 0.002 LOEC = 0.100 IC_{50} = 0.078 LOEC = 0.100	Forney and Davis 1981.

Table C-1. Continued

Species	Test conditions	Temp. (°C)	pH	Hardness (mg $CaCO_3$/L)	Formulation (% active)	LC_{50}/EC_{50} (mg·L^{-1})	Reference
Watermilfoil (*Myriophyllus* sp.)	as above	20°C–30°C	—	—	—	IC_{50} = 0.064 LOEC = 0.032	Forney and Davis 1981.
Duckweed (*Lemna perusilla*)						IC_{50} = 0.016 LOEC = 0.010	
Aquatic and soil algae: *Schizothrix calcicola*, *Anabaena* sp., *Chlorella vulgaris*, *Chlamydomonas* sp., *Chlorococcum* sp.	static, unmeasured, 6 d of growth, *S. calcicola* grown in soil, others in turbulent culture, turbidimetric colourimetry compared to control, LOEC as above					LOEC (each species): 0.05 mg·L^{-1} 0.05 mg·L^{-1} 0.05 mg·L^{-1} 0.05 mg·L^{-1} 0.05 mg·L^{-1}	Arvik et al. 1973.