



Canadian Water Quality Guidelines for the Protection of Agricultural Water Uses

CHLOROTHALONIL

Chlorothalonil is a broad-spectrum fungicide sold under the trade names such as Daconil 2787 and Bravo. Chlorothalonil is used for controlling fungal pathogens in cabbage, broccoli, cauliflower, brussels sprouts, carrots, celery, cucumbers, melons, potatoes, tomatoes, squash, turf, ornamentals, and conifers. It is also used as a preservative in latex paints (Agriculture and Agri-Food Canada 1997).

In neutral and acidic soils, chlorothalonil is relatively immobile and persistent, with a half-life in sandy loam of 1–2 months (Stallard et al. 1972). Little movement ($0.01\text{--}0.17\text{ mg}\cdot\text{kg}^{-1}$) below 0–7.6 cm occurred throughout the 8-month study. Reduker et al. (1988) reported only 2.8% (2.8 mg) was recovered from soil column elution and soil extraction, suggesting either strong adsorption or significant degradation. Capps et al. (1982) concluded that chlorothalonil was moderately mobile in sand and that organic material did not influence its mobility. Krawchuck and Webster (1987) found chlorothalonil in the outflow of tile drains from irrigated cropland ($0.06\text{--}3.66\text{ }\mu\text{g}\cdot\text{L}^{-1}$) and concluded that it was mobile in coarse sandy soils.

For more information on the use, environmental concentrations, and chemical properties of chlorothalonil, see the fact sheet on chlorothalonil in Chapter 4 of *Canadian Environmental Quality Guidelines*.

Water Quality Guideline Derivation

The interim Canadian water quality guidelines for chlorothalonil for the protection of agricultural water uses were developed based on the CCME protocol (CCME 1993).

Irrigation Water

No definitive reports of phytotoxicity have been reported from chlorothalonil use at recommended rates. Agriculture Canada (1985) reported the results of four studies; no toxicity to any of the crops (spring wheat, hard red winter wheat, barley, creeping bent grass, and annual bluegrass) was found at rates of $1.125\text{--}24.0\text{ kg}\cdot\text{ha}^{-1}$.

Discolouration of blooms has been observed in petunias, hydrangeas, azaleas, and rhododendrons when chlorothalonil was applied at concentrations of $1.25\text{ g}\cdot\text{L}^{-1}$

of spray during flowering (ISK Biotech 1990a). The maximum labelled application rate presumed to have been used was $2.5\text{ kg}\cdot\text{ha}^{-1}$. A single application of $14\text{ g}\cdot\text{L}^{-1}$ to mature leaves of greenhouse-grown pecan seedlings (*Carya illinoensis*) reduced net photosynthesis for 9 d post-treatment (Wood et al. 1984). Since this crop is not grown in Canada and an application rate could not be calculated, it was not used for guideline derivation.

Limited phytotoxicity occurred in De Chaunac grapes when two flowable formulations (Bravo 7.2F [$720\text{ g}\cdot\text{L}^{-1}$] and Bravo 500F [$500\text{ g}\cdot\text{L}^{-1}$]) were applied at concentrations equivalent to $1.5\text{ kg}\cdot\text{ha}^{-1}$ per application (Northover and Ripley 1980). A full-season program of six applications was compared to a late-season, three-spray program. The 7.2F and 500F formulations damaged the berries (superficial epidermal roughness, scaling, and blotchy coloration) when assessed 14 d after the final application.

Stephenson et al. (1980) observed additive phytotoxicity to tomato seedlings exposed to chlorothalonil plus metribuzin. Metribuzin was sprayed on day 30 at 0.25 or $0.50\text{ kg}\cdot\text{ha}^{-1}$, and 3 h later Bravo (75WP) was applied to the foliage at $2.52\text{ kg}\cdot\text{ha}^{-1}$. Phytotoxicity was additive as slight injury occurred to plants exposed to metribuzin alone, but significantly greater injury was found in combination with chlorothalonil. Field studies, however, showed no reduction in tomato yield and no enhanced metribuzin injury. The disparity between field and laboratory results was attributed to differences in light intensity.

Sufficient data existed to derive a guideline only for the “other crops” group, which consists of crops other than cereals, tame hays, or pastures. A LOEAR of $1.5\text{ kg}\cdot\text{ha}^{-1}$ was reported for grapes (Northover and Ripley 1980). The NOEAR was estimated by dividing the LOEAR by 4.5,

Table 1. Water quality guidelines for chlorothalonil for the protection of agricultural water uses (CCME 1994).

Use	Guideline value ($\mu\text{g}\cdot\text{L}^{-1}$)
Irrigation water	$5.8^{*\dagger}$
Livestock water	170^*

* Interim guideline.

† Other crops.

resulting in a NOEAR of $0.33 \text{ kg}\cdot\text{ha}^{-1}$. The geometric mean of these values was divided by an uncertainty factor of 10 to arrive at an acceptable application rate (AAR) of $0.07 \text{ kg}\cdot\text{ha}^{-1}$. The AAR was then divided by the approximate Canadian annual irrigation rate of $10^7 \text{ L}\cdot\text{ha}^{-1}$ per year to calculate the SMATC of $5.8 \mu\text{g}\cdot\text{L}^{-1}$. This value is the recommended interim Canadian water quality guideline for irrigation of "other crops" (CCME 1994).

Livestock Water

The acute dermal and oral LD_{50} s for rats and rabbits were $>10\,000 \text{ g}\cdot\text{kg}^{-1}$ (ISK Biotech 1985). Inhalation studies using rats reported a 1-h LC_{50} of $0.31 \text{ mg}\cdot\text{L}^{-1}$ for technical chlorothalonil and 4-h LC_{50} s of 0.54, 0.9, and $>7.16 \text{ mg}\cdot\text{L}^{-1}$ for Daconil 2787 W-75, Bravo W-75, and Bravo 500, respectively (ISK Biotech 1985).

Several studies have evaluated the chronic toxicity of chlorothalonil to mammals such as rats, mice, dogs, and rabbits. Effects measured were renal histopathology, body and organ weights, growth rates, teratogenicity, mutations, mortality, tumour growth, blood chemistry, fertility, pre-implementation losses, and fetal mortality. Kidney damage was generally identified as the likely effect of exposure; the NOEL and LOEL were 1.0 and $1.5 \text{ mg}\cdot\text{kg}^{-1}$ per day, respectively, in a 1-year rat study (Health Canada 1993).

Reproduction effects were assessed in two studies where technical chlorothalonil was fed to Charles River CD rats. ISK Biotech (1990b) reported reduced body weights in F0 and F1 adults at a LOEL of $75 \text{ mg}\cdot\text{kg}^{-1}$ per day and a NOEL of $25 \text{ mg}\cdot\text{kg}^{-1}$ per day. Stomach lesions were found in all animals and kidney lesions in all but males at the lowest dose tested of $25 \text{ mg}\cdot\text{kg}^{-1}$ per day. Decreased pup weight was observed on day 21 of lactation at $300 \text{ mg}\cdot\text{kg}^{-1}$ per day, but not at $150 \text{ mg}\cdot\text{kg}^{-1}$ per day. Paynter and Kundzin (1967) fed chlorothalonil at up to $250 \text{ mg}\cdot\text{kg}^{-1}$ per day to three generations of rats. Significant growth suppression was observed in the nursing litters of each generation. Reproductive performance was not affected, and pups showed no malformations attributable to chlorothalonil. Body weight gains for exposed rats (male and female) were lower than those in control animals (USEPA 1989).

Reported NOELs for maternal toxicity and teratogenicity for rats and rabbits were 100 and $400 \text{ mg}\cdot\text{kg}^{-1}$ per day, respectively (Rodwell et al. 1983). Health Canada (1993) reported a NOEL for embryotoxicity, fetotoxicity, and teratogenicity of $20 \text{ mg}\cdot\text{kg}^{-1}$ per day for New Zealand white rabbits. It was concluded that chlorothalonil is not a mammalian genotoxic agent (Health Canada 1993).

Chlorothalonil is classified as a potential human carcinogen (Group B2) (USEPA 1989). No clear dose-related trend was distinguished. Chlorothalonil was carcinogenic in Osborne-Mendel rats (NCI 1980). Dose-related adenomas and adenocarcinomas of the renal tubular epithelium developed in the treated rats. The observed tumours were considered to be histogenically related and sufficient evidence for carcinogenicity in Osborne-Mendel rats (USEPA 1989). In a 2-year study using the Fisher 344 rat, a NOEL of $1.5 \text{ mg}\cdot\text{kg}^{-1}$ per day and a LOEL of $3.3 \text{ mg}\cdot\text{kg}^{-1}$ per day were reported based on general toxicity and oncogenicity and primary stomach tumours (Health Canada 1993).

When mallard ducklings (*Anas platyrhynchos*) were administered a single dose of $4640 \text{ mg}\cdot\text{kg}^{-1}$ bw of technical chlorothalonil and observed for 8 d, they showed lethargy, lower limb weakness, and reduced body weight gain, but not mortality (ISK Biotech 1977). The single dose LD_{50} for DS-3701 was $158 \text{ mg}\cdot\text{kg}^{-1}$ bw (ISK Biotech 1978). Chronic studies investigating the reproductive effects on mallards and bobwhite quail (*Colinus virginianus*) reported no-observed-effect doses (NOEDs) of 1487 and $100.3 \text{ mg}\cdot\text{kg}^{-1}$ per day, respectively (ISK Biotech 1988a, 1988b). The major degradation product, DS-3701, however, was more toxic. For mallards, the 5-d LD_{50} was $300 \text{ mg}\cdot\text{kg}^{-1}$ per day in ducklings and the lowest-observed-effect dose (LOED) was $15.4 \text{ mg}\cdot\text{kg}^{-1}$ per day based on reduced eggshell thickness of (ISK Biotech 1981b, 1988b). The degradation product DS-3701 was also more toxic in 14-d-old bobwhite quail than the parent compound, with a LOED of $100 \text{ mg}\cdot\text{kg}^{-1}$ per day causing lethargy, loss of the righting reflex, and prostrate posture (ISK Biotech 1981a).

The most sensitive mammal or bird found was the rat, with a reported 1-year LOEL and NOEL of 1.5 and $1.0 \text{ mg}\cdot\text{kg}^{-1}$ per day, respectively (Health Canada 1993). However, a 2-year study conducted in 1987 on the Fischer 344 rat was deemed the most appropriate to derive the recommended human acceptable daily intake (ADI) (C. Warfield 1993, Health Canada, Ottawa, pers. com.). This study reported a LOEL and NOEL of 3.3 and $1.5 \text{ mg}\cdot\text{kg}^{-1}$ per day, respectively, for general toxicity and oncogenicity, and was considered the most appropriate to derive the TDI. To calculate the TDI, the geometric mean of the LOEL and NOEL was divided by an uncertainty factor of 10 to result in a TDI of $0.22 \text{ mg}\cdot\text{kg}^{-1}$ per day. Multiplying the TDI by the ratio of animal body weight to water intake for the most conservative livestock animal (leghorn chicken) yielded an RC of $0.83 \text{ mg}\cdot\text{L}^{-1}$. To account for exposure to chlorothalonil from sources other than water, the lowest RC is multiplied by an apportionment factor of 0.2 to give an interim water

quality guideline of 170 µg·L⁻¹ for the protection of livestock (CCME 1994).

References

- Agriculture and Agr-Food Canada. 1997. Regulatory Information on Pesticide Products (RIPP) Database (CCINFODISK). Issue 97-3. Produced by Agriculture and Agri-Food Canada and distributed by the Canadian Centre for Occupational Health and Safety. CD-ROM.
- Agriculture Canada. 1985. Pesticide research report: 1985. Compiled by the Expert Committee on Pesticide Use in Canada, Ottawa.
- Capps, T.M., J.P. Marcinişzyn, A.F. Marke, and J.A. Ignatoski. 1982. Document No. 555-4EF-81-0261-001, Section J, Vol. VI. Submitted by Diamond Shamrock Corporation. (Cited in USEPA 1989.)
- CCME (Canadian Council of Ministers of the Environment). 1993. Appendix XV—Protocols for deriving water quality guidelines for the protection of agricultural water uses (October 1993). In: Canadian water quality guidelines, Canadian Council of Resource and Environment Ministers. 1987. Prepared by the Task Force on Water Quality Guidelines. [Updated and reprinted with minor revisions and editorial changes in Canadian environmental quality guidelines, Chapter 5, Canadian Council of Ministers of the Environment, 1999, Winnipeg.]
- . 1994. Appendix XVII—Canadian water quality guidelines: Updates (March 1994), chlorothalonil. In: Canadian water quality guidelines, Canadian Council of Resource and Environment Ministers. 1987. Prepared by the Task Force on Water Quality Guidelines.
- Health Canada. 1993. Health Protection Branch evaluation report on chlorothalonil. Health Protection Branch, Ottawa. Unpub.
- ISK Biotech. 1977. Acute oral LD₅₀ in mallard duck with DS-2787. 000-5TX-77-0111-001. ISK Biotech Corporation, Mentor, OH.
- . 1978. Acute oral LD₅₀ in mallard ducks with DS-3701. 00-5TX-77-0119-001. ISK Biotech Corporation, Mentor, OH.
- . 1981a. Dietary study (LC₅₀) in bobwhite quail with DS-3701. 448-5TX-81-0007-002. ISK Biotech Corporation, Mentor, OH.
- . 1981b. Dietary study (LC₅₀) in mallard ducks with DS-3701. 449-5TX-81-0008-002. ISK Biotech Corporation, Mentor, OH.
- . 1985. BRAVO/DACONIL 2787 Broad spectrum fungicide. ISK Biotech Corporation, Mentor, OH.
- . 1988a. Reproduction study in mallard ducks with technical chlorothalonil. 1469-87-0004-TX-002. ISK Biotech Corporation, Mentor, OH.
- . 1988b. Reproduction study in mallard ducks with 4-hydroxy-2,5,6-trichloroisophthalonitrile (ISK-3701). 1418-96-0064-TX-002. ISK Biotech Corporation, Mentor, OH.
- . 1990a. BRAVO/DACONIL 2787: Broad-spectrum fungicide. General information booklet. ISK Biotech Corporation, Mentor, OH.
- . 1990b. A two generation reproduction study in rats with technical chlorothalonil. 1722-87-0121-TX-003. ISK Biotech Corporation, Mentor, OH.
- Krawchuk, B.P., and G.R.B. Webster 1987. Movement of pesticides to ground water in an irrigated soil. *Water Pollut. Res. J. Can.* 22(1):129–146.
- NCI (National Cancer Institute). 1980. Bioassay of chlorothalonil for possible carcinogenicity. NTP #TR-041. U.S. Public Health Service, U.S. Department of Health, Education and Welfare. (Cited in USEPA 1989.)
- Northover, J. and B. Ripley. 1980. Persistence of chlorothalonil on grapes and its effect on disease control and fruit quality. *J. Agric. Food Chem.* 28:97–1974.
- Paynter, O.E., and M. Kundzin. 1967. Final report: Three-generation reproduction study: Rats. Project No. 200-155. study. MRID 00091289. Unpub. (Cited in USEPA 1989.)
- Reduker, S., C.G. Uchirin, and G. Winnett. 1988. Characteristics of the sorption of chlorothalonil and azinphos-methyl to a soil from a commercial cranberry bog. *Bull. Environ. Contam. Toxicol.* 41(5):633–641.
- Rodwell, D., M. Mizens, N. Wilson et al. 1983. A teratology study in rats with technical chlorothalonil. Document No. 517-5TX-82-0011-003. Submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH. Unpub. (Cited in USEPA 1989.)
- Stallard, D.E., A.L. Wolfe, and W.C. Duane. 1972. Evaluation of the leaching of chlorothalonil under field conditions and its potential to contaminate underground water supplies. Submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH. Unpub. (Cited in USEPA 1989.)
- Stephenson, G.R., S.C. Phatak, R.I. Makowski and W.J. Bouw. 1980. Phytotoxic interactions involving metribuzin and other pesticides in tomatoes. *Can. J. Plant Sci.* 60:167–175.
- USEPA (U.S. Environmental Protection Agency). 1989. Drinking Water Health Advisory: Pesticides. Office of Drinking Water Health Advisories. Lewis Publishers, Inc., Chelsea, MI.
- Wood, B., T. Gottwald, and J. Payne. 1984. Influence of single applications of fungicides on net photosynthesis of pecan. *Plant Dis.* 68:427–428.

Reference listing:

Canadian Council of Ministers of the Environment. 1999. Canadian water quality guidelines for the protection of agricultural water uses: Chlorothalonil. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

For further scientific information, contact:

Environment Canada
Guidelines and Standards Division
351 St. Joseph Blvd.
Hull, QC K1A 0H3
Phone: (819) 953-1550
Facsimile: (819) 953-0461
E-mail: ceqg-rcqe@ec.gc.ca
Internet: <http://www.ec.gc.ca>

For additional copies, contact:

CCME Documents
c/o Manitoba Statutory Publications
200 Vaughan St.
Winnipeg, MB R3C 1T5
Phone: (204) 945-4664
Facsimile: (204) 945-7172
E-mail: spcme@chc.gov.mb.ca