Canadian Water Quality Guidelines for the Protection of Aquatic Life

CHLOROTHALONIL

Chlorothalonil ($C_8Cl_4N_2$) is a nonsystemic foliar fungicide with a CAS name and number of 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile and 1897-45-6, respectively (Tomlin 1994). Chlorothalonil was initially registered in 1966 under the trade names Daconil 2787, Bravo, Nopocide, Nuocide, C-I-L, and Exotherm Termil Protectant Fungicide Formulation.

Chlorothalonil is used for controlling fungal pathogens in cabbage, broccoli, cauliflower, brussel 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).

Chlorothalonil is used primarily in New Brunswick, Nova Scotia, Prince Edward Island, Ontario, and Manitoba. In 1992, 7565 kg a.i. were sold in New Brunswick (K. Browne 1993, New Brunswick Environment, pers. com.). In 1988, 78 470 kg of chlorothalonil were used in Ontario (Moxley 1989). In 1982, 5120 kg a.i. were used in New Brunswick, while 1150 and 23 520 L were used in Nova Scotia and Prince Edward Island, respectively (Monenco 1984).

Chlorothalonil contamination of the aquatic environment may occur from direct application or indirectly from processes such as spray drift and runoff. Reported concentrations of chlorothalonil in Canadian waters range from 0.005 $\mu g \cdot L^{-1}$ (O'Neill et al. 1992) to 272.2 $\mu g \cdot L^{-1}$ (Krawchuk and Webster 1987).

Davies (1988) examined the influence of fish, algae, temperature, solute concentration, and aeration on the fate of chlorothalonil in stream water. Davies (1988) found that 64.4–95.2% of the original 20 $\mu g \cdot L^{-1}$ was associated with particulate matter. Loss from the water increased with higher temperature, both for still stream water and when aerated in the presence of rocks and algae. A rise from 5 to 15ºC decreased the half-life in still water from 150 to 80 h and in aerated water from 13.9 to 7.7 h, respectively. The effect of aeration alone (no rocks or algae) increased the half-life from 80 to 101.3 h in 15ºC stream water, which suggests that chlorothalonil adsorbed to suspended particulate does not volatilize when aerated. This is supported by its low air–water partition coefficient of 8.0×10^{-6}, indicating that the amount in the vapour phase would be small (Kawamoto and Urano 1989).

The disappearance of chlorothalonil and appearance of polar metabolites in solution was significantly enhanced by the presence of algae and fish. Residue analysis of the algae showed a bioconcentration factor of 270, which represented 9.5% of the initial exposure concentration. The average rate of degradation was estimated at 3.4 $\mu g \cdot h^{-1} \cdot g^{-1}$ ww algae. When fish *(Galaxias auratus)* were present, the rate of loss was enhanced 25 times, and the rate of appearance of polar metabolites (presumed to be predominantly DS-3701) increased threefold. The lowest half-life values reported were for aerated water and fish (4.3 h) and for aerated water, rocks, and algae (4.4 h) (Davies 1988).

In water of pH <8.0, hydrolysis is insignificant. At pH values >8.0, hydrolysis occurs at 1.8% per day Chlorothalonil was hydrolyzed to DS-3701 and 3-cyano-2,4,5,6-tetrachlorobenzamide in water of pH 9.0 with a calculated half-life of 38.1 d (Szalkowski and Stallard 1977). Ernst et al. (1991) estimated the half-life to be 30 h in soft water with pH values between 6.5 and 7.4 and total hardness of 12.3 $mg \cdot L^{-1}$.

ISK Biotech (1991) conducted an aerobic metabolism study in fresh and marine waters with sediment (9:1 ratio) at 25ºC and a concentration of 600 $\mu g \cdot L^{-1}$ chlorothalonil. The degradation was nonlinear, with a DT_{50} (time to 50% dissipation) of < 2 h, but residues persisted, with approximately 1.6% (9.5 $\mu g \cdot L^{-1}$), for freshwater, and 2.6% (16 $\mu g \cdot L^{-1}$), for marine water, of the originally applied dose detectable as parent compound after 30 d. Walker et al. (1988) examined the biotic and abiotic degradation in estuarine water in vitro and sediment/water systems. The fate in simulated marine environments was similar to that in freshwater systems. Chlorothalonil half-lives were

Table 1. Water quality guidelines for chlorothalonil for the protection of aquatic life (CCME 1994).

Aquatic life	Guideline value ($\mu g \cdot L^{-1}$)
Freshwater	0.18*
Marine	0.36*

*Interim guideline

10 d, 8–9 d, and 3 d in sterile water, nonsterile water, and nonsterile sediment-slurry, respectively. These results suggest that microbial activity is a major process in the breakdown of chlorothalonil in marine environments.

Water Quality Guideline Derivation

The interim Canadian water quality guidelines for chlorothalonil for the protection of freshwater life were developed based on the CCME protocol (CCME 1991).

Freshwater Life

Acute toxicity (96-h LC_{50}) values for fish ranged from 10.5 to 195 µg·L^{-1} for rainbow trout *(Oncorhynchus mykiss)* (Davies 1987; ISK Biotech 1990). Flow-through toxicity tests with *O. mykiss* illustrated that lowering the dissolved oxygen concentration from 8.0 to 5.1 mg·L^{-1} had a synergistic effect on toxicity by significantly reducing the 96-h LC_{50} from 17.1 to 10.5 µg·L^{-1} (Davies 1987).

In chronic studies, Davies and Cook (1986) exposed *O. mykiss* and the native Australian freshwater sandy (*Pseudaphritis urvillii*) to up to 8.2 µg·L^{-1} for 10 d. In rainbow trout, RNA and DNA levels were significantly depressed at 8.2 µg·L^{-1}, while hepatic glutathione (GSH) was elevated at ≥1.4 µg·L^{-1}. A LOEC of 1.4 µg·L^{-1} based on elevated glutathione S-transferase (GST) activity was reported, but decreased to control levels at 8.2 µg·L^{-1}. The reported LOEC for the sandy based on increased oxygen demand was 0.3 µg·L^{-1}.

ISK Biotech (1989a) determined a 21-d LOEC and NOEC of 4.9 and 2.3 µg·L^{-1}, respectively, for mortality and behavioural effects of formulated chlorothalonil (40.4% ai) to *O. mykiss*. Similar results were obtained by Davies (1987) who concluded that chronic exposure to low levels of chlorothalonil (1–5 µg·L^{-1}) seriously impaired gill function. Exposure of fathead minnows over one full life cycle (egg to egg) resulted in a significant decrease in the number of eggs per spawn, egg hatchability, and fry survival at concentrations ≥6.5 µg·L^{-1} (LOEC) and a NOEC 3.0 µg·L^{-1} (reproduction) (ISK Biotech 1980).

The sensitivities for invertebrates ranged from 1.8 µg·L^{-1} to >10 000 µg·L^{-1}. The most sensitive invertebrate was *Daphnia magna* with a 22-d LOEC and NOEC of 1.8 and 10 000 µg·L^{-1}, respectively, for immobilization using formulated chlorothalonil (ISK Biotech 1989b).

The freshwater shrimp *Paratya australiensis*, freshwater lobster *Astacopsis gouldi*, isopod *Colubotelson chiltoni minor*, and amphipod *Neoniphargus* sp. were exposed to concentrations ranging from 0.3 to 38.5 µg·L^{-1} resulting in 7-d LC_{50} values of 10.9, 3.6, >40, and >40 µg·L^{-1}, respectively (Davies and Cook 1986). The MATC was between 0 and 0.3 µg·L^{-1} for the freshwater shrimp based on elevated whole body GST levels.

For algae, a 96-h LC_{50} of 525 µg·L^{-1} and a LOEC of 160 µg·L^{-1} for *Scenedesmus subspicatus* were reported using formulated Daconil 2787 Extra (ISK Biotech 1989c). Ernst et al. (1993) found a 7-d IC_{50} value of 8500 µg·L^{-1} for *Selenastrum capricornutum*.

The two most sensitive species identified in the literature were the sandy, with a LOEC of 0.3 µg·L^{-1}, and the rainbow trout, with a LOEC of 1.4 µg·L^{-1} (Davies and Cook 1986). The sandy does not occur in Canada and there is some controversy over whether the toxicity endpoints used for the rainbow trout (GST activity) constitute a valid toxicological endpoint. In light of this, the next most sensitive species was *D. magna*, with a 22-d LOEC of 1.8 µg·L^{-1} (ISK Biotech 1989b). Multiplying this value by a safety factor of 0.1 for chronic studies results in an interim water quality guideline for chlorothalonil for the protection of freshwater life of 0.18 µg·L^{-1} (CCME 1994). This value refers to the total concentration of chlorothalonil and its 4-hydroxy transformation product (DS-3701).

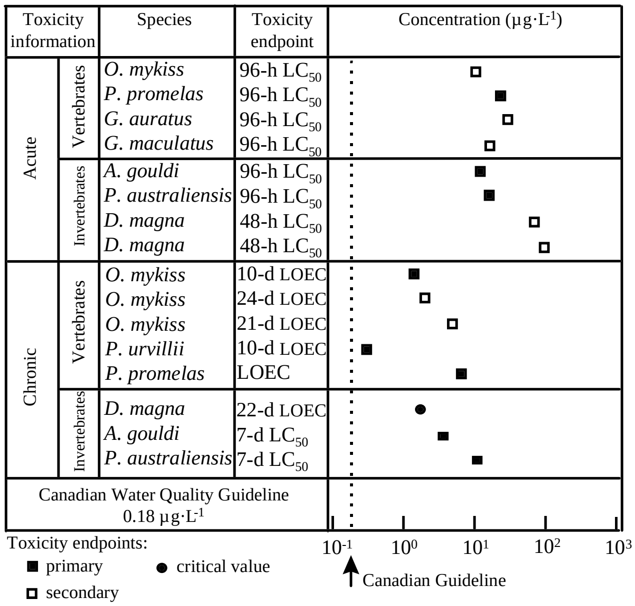

Figure 1. Select freshwater toxicity data for chlorothalonil.

Marine Life

The acute toxicity (96-h LC_{50}) values for fish ranged from 27 to 4700 $\mu g\cdot L^{-1}$ for the three-spine stickleback (Ernst et al. 1993). Acute data values for invertebrates ranged from a 96-h EC_{50} of 7.3 $\mu g\cdot L^{-1}$, based on reduced shell growth for the eastern oyster *(Crassostrea virginica)* (ISK Biotech 1983), to a 96-h+10-d LC_{50} of 34 780 $\mu g\cdot L^{-1}$ for the soft-shell clam (Ernst et al. 1991). Both chlorothalonil and DS-3701 were relatively nontoxic to the bacterium *Photobacterium phosphoreum* in the Microtox test (Ernst et al. 1993). The 30-min IC_{50} values were >25 000 $\mu g\cdot L^{-1}$ and 75 000 < IC_{50} < 150 000 $\mu g\cdot L^{-1}$, respectively.

The interim water quality guideline for chlorothalonil for the protection of marine life is 0.36 $\mu g\cdot L^{-1}$ (CCME 1994). It was derived by multiplying the 96-h EC_{50} of 7.3 $\mu g\cdot L^{-1}$ for the eastern oyster (reduced shell growth) (ISK Biotech 1983) by a safety factor of 0.05 (acute study, non-persistent substance) (CCME 1991).

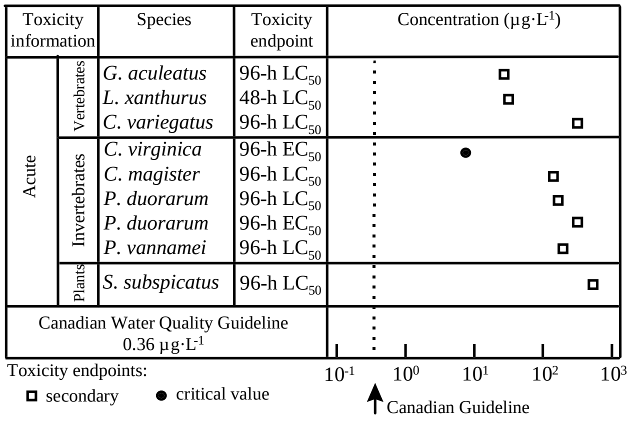

Figure 2. Select marine toxicity data for chlorothalonil.

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