Canadian Water Quality Guidelines for the Protection of Agricultural Water Uses

CHLORPYRIFOS

Chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$), also known as chlorpyrifos-ethyl, is a broad spectrum organophosphate insecticide. It has a CAS name and registry number of *o, o*-diethyl-*o*-(3, 5, 6-trichloro-2-pyridinyl) phosphorothioate and 2921-88-2, respectively. Chlorpyrifos is a colourless crystalline solid that is manufactured under numerous trade names including Dursban and Lorsban.

Chlorpyrifos is registered for use in agriculture to control numerous insects on barley, wheat, oats and a wide variety of garden vegetables (Agriculture Canada and Environment Canada 1990; Agriculture and Agri-Food Canada 1997). Nonagricultural uses include the control of insect pests on turf and ornamental plants and in nonfood domestic areas, veterinary clinics, and commercial storage or processing sites (Agriculture and Agri-Food Canada 1997).

Chlorpyrifos may be applied dermally, ingested, or inhaled and is metabolized to its active form, chlorpyrifos oxon. In insects, chlorpyrifos oxon phosphorolyzes the active site of acetylcholinesterase (AChE) and thereby disrupts normal nerve impulse transmission, leading to overstimulation of the peripheral nervous system and, ultimately, convulsions, paralysis, and death (Barron and Woodburn 1995).

Chlorpyrifos is readily absorbed, metabolized, and eliminated by most vertebrates (Key and Fulton 1993). For example, cattle fed 3 $mg \cdot kg^{-1}$ per day chlorpyrifos for 30 d had chlorpyrifos plus metabolite residues of 3,5,6-trichloro-2-pyridinol (TCP) <0.01, 0.08, 0.23, and 0.15 $mg \cdot kg^{-1}$ in muscle, fat, liver, and kidneys, respectively (Dishburger et al. 1977). Lactating Holstein dairy cows fed 30 $mg \cdot kg^{-1}$ chlorpyrifos for 14 d had maximum chlorpyrifos plus TCP residues of 0.02 and 0.1 $mg \cdot L^{-1}$ in milk and cream, respectively (McKellar et al. 1976). Swine fed 10 $mg \cdot kg^{-1}$ had chlorpyrifos plus TCP residues of 0.03, 0.39, 0.32, 0.16 $mg \cdot kg^{-1}$ in muscle, fat, liver, and kidneys, respectively (McKellar et al. 1972). Chickens given feed treated with 10 $mg \cdot kg^{-1}$ chlorpyrifos for 30 d retained maximum chlorpyrifos plus TCP residues of <0.01, 0.06, 0.25, 0.84 $mg \cdot kg^{-1}$ in muscle and eggs, fat, liver, and kidneys, respectively (Dishburger et al. 1972). However, chlorpyrifos residues up to 11 $mg \cdot kg^{-1}$ lipid were detected in 430 of 832 wings of wild, free-ranging bobwhite quail *(Colinus virginianus)* in Virginia state between 1982 and 1986 (Stinson et al. 1989).

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

Water Quality Guideline Derivation

The interim Canadian water quality guideline for chlorpyrifos for the protection of livestock water was developed based on the CCME protocol (CCME 1993).

Livestock Water

Chlorpyrifos is moderately toxic to mammals, with acute oral LD_{50}s ranging from 62 to 504 $mg \cdot kg^{-1}$ for mice and guinea pigs, respectively (Taylor and Olsen 1963; McCollister et al. 1974). Acute oral LD_{50} values for female rats vary from 82 to 155 $mg \cdot kg^{-1}$, while those for male rats are 118–245 $mg \cdot kg^{-1}$ (Gaines 1969; McCollister et al. 1974). Adult rats injected subcutaneously with 280 $mg \cdot kg^{-1}$ chlorpyrifos experienced a short-term depression of body core temperature, prolonged heart rate elevation, and long-term depression of brain and plasma cholinesterase (ChE) activity. The subcutaneous LD_{50} for 1-d-old rats is 5–11 $mg \cdot kg^{-1}$ (Whitney et al. 1995). Rat pups, 3, 10, or 12 d old administered Dursban intraperitoneally at 0.1 or 0.3 $mg \cdot kg^{-1}$ per day displayed no adverse effects in behaviour or motor skills (Muto et al. 1992). At the higher rate, however, all age groups experienced neurotoxicity. In Sprague-Dawley rats, dosed with 50 $mg \cdot kg^{-1}$ per day chlorpyrifos, serum ChE and aminopyrine N-demethylase activity decreased 82 and 18%, respectively, while microsomal protein, cytosolic glutathione S-transferase activity (GST), and cytochrome P_{450} increased 19, 54, and 18%, respectively (Vodela and Dalvi 1995). The increase in GST activity suggests that GST mediates the detoxification of chlorpyrifos.

Table 1. Water quality guidelines for chlorpyrifos for the protection of agricultural water uses (CCME 1997).

Use	Guideline value ($\mu g \cdot L^{-1}$)
Irrigation water	NRG*
Livestock water	24†

*No recommended guideline.

†Interim guideline.

Acute oral toxicity data are also available for numerous bird species. Single acute oral LD_{50} values for chlorpyrifos range from 3.2 $mg \cdot kg^{-1}$ for red-winged blackbirds *(Agelaius phoeniceus)* to 157 $mg \cdot kg^{-1}$ for ringed turtle doves *(Streptopelia risoria)* (Schafer 1972; Hill and Camardese 1986). The chicken *(Gallus gallus)* is the most sensitive livestock species, with an oral LD_{50} of 25 $mg \cdot kg^{-1}$ for chicks (Sherman et al. 1967). Mallard ducks *(Anas platyrhynchos)* have 5-d LOECs of 0.3 $mg \cdot kg^{-1}$ for inhibition of blood AChE activity and 9.9 $mg \cdot kg^{-1}$ for food consumption and weight gain (Shellenberger 1970). Horned larks *(Eremophilia alpestris)* collected from wheat fields sprayed with 0.56 or 1.0 $kg \cdot ha^{-1}$ chlorpyrifos suffered 23 and 18% reductions in brain ChE activities 3 and 9 d post-application, respectively (McEwen et al. 1986). Cold stress intensifies chlorpyrifos-induced inhibition of AChE activity in juvenile bobwhite quail, but does not affect survival (Maguire and Williams 1987).

Subchronic and chronic data are available for dairy cattle, dogs, rats, and several bird species. Lactating Jersey cows fed corn for 7 weeks that had been sprayed in the field with Dursban emulsifiable concentrate at rates of 0.3–1.1 $kg \cdot ha^{-1}$, consumed averages of 0.04–0.17 $mg \cdot kg^{-1}$ per day chlorpyrifos. At these rates, no change in milk production occurred, although at 0.17 $mg \cdot kg^{-1}$ per day, ChE activity decreased slightly (Johnson et al. 1969). The dietary 2-year NOEL and LOEL for reduced plasma ChE activity are 0.03 and 0.1 $mg \cdot kg^{-1}$ per day, respectively, for beagle dogs and 0.1 and 1 $mg \cdot kg^{-1}$ per day, respectively, for albino rats (McCollister et al. 1974). Similarly, male and female rats have 2-year NOELs of 0.1 $mg \cdot kg^{-1}$ per day for body weight, food consumption, hematology, clinical chemistry and electrolytes, plasma, brain and erythrocyte ChE depression, urinalysis, and gross and histopathic examination of tissues (Young and Grandjean 1988). The LOEL is 1.0 $mg \cdot kg^{-1}$ per day for male and female rats, though males experienced body weight gain and depression of plasma and erythrocyte ChE activity, while females experienced only depression of plasma ChE activity (Young and Grandjean 1988). The bird species most tolerant to dietary chlorpyrifos exposure is the northern bobwhite quail, with a 28-d LC_{50} of 1100 $mg \cdot kg^{-1}$ chlorpyrifos feed (Shirazi et al. 1994). Chickens have a 21-d LOEC for weight gain of 200 $mg \cdot kg^{-1}$ chlorpyrifos feed and a 32-week NOEL for body and liver weight of 1 $mg \cdot kg^{-1}$ (Sherman et al. 1967; Miyazaki and Hodgson 1972). Mallard ducks aged 7 months, 11 months, and adult experienced reductions in weight, egg production, eggshell thickness, egg weight, and brain AChE activity when given feed treated with 80 $mg \cdot kg^{-1}$ of chlorpyrifos for up to 1 year (Gile and Meyers 1986).

The toxicity of chlorpyrifos to mammalian fetuses is most severe when exposure occurs early in the pregnancy. For example, Dursban administered intraperitoneally to pregnant rats at rates of 0.03–0.3 $mg \cdot kg^{-1}$ per day on days 0 through 7 of gestation, increased mortality (up to 75%) and the number of physical abnormalities (up to 65%) in pups. However, when similarly administered on days 7 through 21 of gestation, pup mortality ranged from 17 to 38%, and physical abnormalities occurred only at the highest rate (Muto et al. 1992). Pregnant mice dosed with 25 $mg \cdot kg^{-1}$ per day chlorpyrifos on days 6 through 15 of gestation experienced severe maternal toxicity, though only minor skeletal variants and decreased body measurements occurred in fetuses (Deacon et al. 1980). Quast et al. (1993) reported NOELs of 5.0, 1.0, and 0.1 $mg \cdot kg^{-1}$ per day chlorpyrifos for reproductive, neonatal, and parental toxicity, respectively. The EC_{50}s for the inhibition of rat embryo midbrain culture differentiation are 29 $mg \cdot L^{-1}$ for formulated chlorpyrifos, and 16–22 $mg \cdot L^{-1}$ for technical grade chlorpyrifos (Cosenza and Bidanset 1995).

Sufficient data are available to derive an interim Canadian water quality guideline for the protection of livestock water. A TDI was calculated for each species for which suitable toxicological data were available. The TDI is the geometric mean of the LOEL and the NOEL divided by an uncertainty factor. The lowest toxicologically significant TDI of 0.032 $mg \cdot kg^{-1}$ per day was calculated for rats having a LOEL and NOEL of 1.0 and 0.1 $mg \cdot kg^{-1}$ per day, respectively, for reduced ChE activity (Young and Grandjean 1988). As it is an interim guideline, an RC was derived by multiplying this TDI for rats by the lowest ratio of body weight to water intake rate, that of leghorn chickens (3.8). To account for exposure to chlorpyrifos from sources other than water, the lowest RC (0.12 $mg \cdot L^{-1}$) is multiplied by an apportionment factor of 0.2 to give an interim water quality guideline of 24 $\mu g \cdot L^{-1}$ for the protection of livestock (CCME 1993, 1997).

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