Canadian Water Quality Guidelines for the Protection of Aquatic Life

CHLORPYRIFOS

Chlorpyrifos (CAS Registry Number 2921-88-2) is an organophosphate insecticide, acaricide, and nematicide. Its chemical formula is $C_9H_{11}NO_3PSCl_3$ and its chemical name is O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate. Chlorpyrifos is an amber to white, crystalline solid with a molecular weight of 350.6 (Mackay et al. 1999).

Chlorpyrifos was introduced in 1965 by Dow Chemical Company. It is currently produced by Dow Chemical Company, India Medical Corp., Makhteshim-Agan (Israel), and Planter Products, Inc. Chlorpyrifos is registered for use in over 30 products sold under trade/product names such as Dursban, Lorsban, Brodan, Detmol UA, Dowco 179, and Empire (Eisler 2000; EXTOXNET 1996). It is formulated as an emulsifiable concentrate, wettable powder, granule, and microencapsulated formulations.

Uses: Chlorpyrifos was originally used to control pests associated with turfgrass, ornamentals, and indoor environments (EPA 1997; PMRA 2000). Through the 1970s, agricultural applications for chlorpyrifos were developed, including its use on grains, field (e.g., corn, tobacco), fruit, nut and vegetable crops.

The use of chlorpyrifos has changed drastically over the last ten years. Residential/homeowner use has been discontinued as has commercial uses around residential area. Agricultural applications have been reduced. The Pest Management Regulatory Agency (PMRA) will undertake a refined environmental risk assessment by 2008 and will make a final decision on the acceptability for continuing registration of chlorpyrifos after that assessment is completed (PMRA 2007).

Sources to the environment: Direct application of chlorpyrifos to soil, vegetation, and animals can result in exposure to non-target organisms. To control mosquitoes, chlorpyrifos may be applied to temporary pools and flooded areas; application to permanent water bodies is not permitted. The application of chlorpyrifos to temporary or flooded areas, along with accidental spillage, spray drift, leaching and runoff from terrestrial applications has the potential to expose aquatic biota to residues.

Fate, behaviour and partioning: Chlorpyrifos is moderately soluble in water, with a solubility of 2 $mg•L^{-1}$ at 25ºC (Kidd and James 1991; Mackay et al. 1999). Jarvinen and Tanner (1982) reported a laboratory half-life of 41 days for chlorpyrifos in solution at water solubility (1-2 $mg•L^{-1}$). The major routes of chlorpyrifos transformation are aerobic and anaerobic biodegradation, while phototransformation is not an important transformation process (PMRA 2000). Temperature and pH influence chlorpyrifos hydrolysis rates in water, as the rate of hydrolysis increases with increases in both temperature and pH. For instance, hydrolysis half-lives of 73, 77, and 16 days were reported for chlorpyrifos at pH 5 and 7 and 9, respectively (PMRA 2000). The major transformation products of chlorpyrifos in water are 3,5,6-trichloro-2-pyridinol (TCP) and O-ethyl O-(3,5,6-trichloro-2-pyridinol)phosphorothionate (PMRA 2000).

Numerous factors influence soil half-life, such as soil moisture content, microbial activity, and clay and organic content (Eisler 2000). These factors result in a wide range of chlorpyrifos half-lives in soil from <1 week to more than 24 weeks (Eisler 2000). Volatilization from moist soils and surface water is expected, based on a Henry's Law constant of 2.9×10^{-4} $kPa•m^3•mol^{-1}$ (Rice and Chernyak 1995). A vapour pressure of 3.33×10^{-6} kPa suggests that chlorpyrifos is unlikely to volatilize from dry soils. The high soil adsorption coefficient (log K_{oc} = 1.61-4.72) and moderate water solubility of chlorpyrifos indicate that it will adsorb to most soils and have low mobility. In addition, these factors limit the persistence of

Table 1. Canadian Water Quality Guidelines for Chlorpyrifos for the Protection of Aquatic Life ($\mu g\ a.i.\cdot L^{-1}$)

	Long-Term Exposure	Short-Term Exposure
Freshwater	0.002*	0.02**
Marine	0.002***	NRG

* value calculated from low-effect data using lowest endpoint approach
** value calculated from LC_{50} data using the SSD approach
*** 1997 marine guideline value
NRG = no recommended guideline

chlorpyrifos in the water column (HSDB 1999; ATSDR 1997).

The log octanol/water partition coefficient (log K_{ow} = 3.31 to 5.27) of chlorpyrifos indicates an affinity for lipids and thus a potential for bioaccumulation in aquatic organisms Bioconcentration factors (BCF) reported for aquatic organisms exposed to chlorpyrifos under field conditions range from 100 to 4,667, and those under laboratory conditions range from 58 to 5,100 (Racke 1993). The degree that chlorpyrifos will bioconcentrate varies with species, exposure duration, and dose. Factors that contribute bioconcentration include metabolic rate, depuration rate, the bioavailability of chlorpyrifos, and the availability of food (Eisler 2000). The BCF values for chlorpyrifos suggest a moderate to very high potential for bioconcentration in fish (Franke et al. 1994).

Under field conditions, chlorpyrifos is non-persistent in the water column. Various field studies from Canada, the United States, and The Netherlands have reported half-lives in aquatic ecosystems from <1 to 3 days (Racke 1993). The short persistence of chlorpyrifos under field conditions is due to its volatility in water, low water solubility, and strong affinity for sediments and suspended solids (ATSDR 1997). Sediment-water half-lives for chlorpyrifos range from 1.2 to 34 days (Schimmel et al, 1983).

Analytical methods: Gas chromatography is typically used to determine sample concentrations of chlorpyrifos, the chlorpyrifos oxygen analog, and 3,5,6-trichloro-2-pyridinol (TCP) (ATSDR 1997). Thin-layer chromatography and high-performance liquid chromatography can also be used. These methods are used in conjunction with selective detection such as flame photometric detection, nitrogen phosphorus thermionic detection, or electron capture detection (ATSDR 1997). The determination of chlorpyrifos concentrations in environmental media begins with liquid/liquid extraction, solid phase extraction (SPE), or Soxhlet extraction. Recoveries from natural waters using SPE can be reduced by the presence of humic material (ATSDR 1997). Further extraction and purification can be accomplished using SPE, gel permeation chromatography, florisil column chromatography, or sweep co-distillation (ATSDR 1997).

Ambient concentrations: Canada's first nation-wide water surveillance project for pesticides was initiated in 2003 by Environment Canada as part of the Pesticide Science Fund. The initiative has been conducted independently in five regions of Canada (Pacific Yukon Region, Prairie and Northern Region, Ontario Region, Quebec Region, and Atlantic Region) and includes monitoring for chlorpyrifos levels. Samples from the Environment Canada Pacific Yukon Region were collected in areas of high pesticide use following storm events. A total of 140 surface water samples were taken and chlorpyrifos was detected in 56 of these samples. Concentrations ranged from <0.0000005 µg a.i.•L^{-1} to 0.0183 µg a.i.•L^{-1} (method detection limit= 0.0000005 µg a.i.•L^{-1})(CEI 2006).

Chlorpyrifos was detected in <50% of samples taken in the spring and summer from five reservoirs in Saskatchewan and Alberta, monitored during 2003/2004 in the Prairie Northern Region. Most of the reservoir catchments sampled were seeded to crops. The detection limit used with these samples was not reported.

A maximum concentration of 0.055 µg a.i.•L^{-1} was reported for nine samples taken in the Ontario Region in 2003/2004, and 0.205 µg a.i.•L^{-1} for 160 samples in 2004/2005. These results did not distinguish between samples from agricultural or urban areas. Sampling in the Quebec Region focuses on the tributaries entering the St. Lawrence River. Samples from the St. François River ranged from <0.02 to 0.13 µg a.i.•L^{-1}. Chlorpyrifos concentrations in samples from the St. Lawrence River were <0.006 µg a.i.•L^{-1}. The proximity of the sampling locations to sources of chlorpyrifos is not reported.

Mode of action: The primary mechanism of toxicity for organophosphorus pesticides, like chlorpyrifos, is cholinesterase (ChE) inhibition. The inhibition of the enzyme acetylcholinesterase (AChE) results in the buildup of acetylcholine (ACh) at choline receptors, causing continual nerve stimulation (Giesy et al, 1999). Chlorpyrifos is a relatively weak AChE inhibitor compared to its metabolite chlorpyrifos oxon (El-Merhibi et al, 2004), thus toxicity is initiated by the formation of chlorpyrifos oxon by oxidative desulfuration (Eisler 2000; Giesy et al. 1999). Factors influencing the toxicity of chlorpyrifos between species and groups include metabolic rate, the number of target sites available for chlorpyrifos metabolism to chlorpyrifos oxon (Chambers and Carr 1995), organism surface area, and lifestage (El-Merhibi et a*l*. 2004).

Freshwater Toxicity: Vertebrates are generally more tolerant of short-term and long-term exposure than invertebrates (Giesy et a*l*, 1999). Symptoms of chlorpyrifos toxicity include motor incoordination, delayed maturation and growth, scoliosis, renal histopathology, and reproductive impairment (Eisler 2000).

Toxicity values reported in the literature for freshwater fish ranged from a 96-hLC_{50} of 1.3 µg a.i.•L^{-1} for bluegill sunfish (*Lepomis macrochirus*) to a 72-h LC_{50} of 2,600 µg a.i.•L^{-1} for mosquitofish (*Gambusia affinis*) (EFED 2005; Davey et al. 1976).

Temperature has been observed to affect the short-term toxicity of chlorpyrifos to fish. In a study examining the effect of temperature on chlorpyrifos toxicity, 96-h LC_{50}s for juvenile rainbow trout (*Oncorhynchus mykiss*) were 7.1, 15, and 51 µg a.i.•L^{-1} at temperatures of 12.7, 7.2, and 1.6ºC, respectively (Macek et al. 1969).

A comparison of chlorpyrifos toxicity to different life stages of walleye (*Stizostedion vitreum*) identified post larvae II as the most sensitive with 48-h LC_{50}s of 12 and 13 µg a.i.•L^{-1} reported for species from two different hatcheries (Phillips et a*l*, 2002). Ninety-six hour LC_{50} values for fathead minnows (*Pimephales promelas*) ranged from 120 to 542 µg a.i.•L^{-1} (Jarvinen and Tanner 1982; Phipps and Holcombe 1985). At concentrations ≥47 µg a.i.•L^{-1}, effects to schooling behaviour were observed after 24 hours of exposure (e.g., location, orientation, grouping pattern), and spinal deformities were apparent after 48 hours of exposure (Holcombe et al. 1982).

Sublethal effects were monitored in coho salmon (*Oncorhynchus kisutch*) exposed to 0.6, 1.2, 1.8, and 2.5 µg a.i./L of chlorpyrifos. Spontaneous swimming was significantly reduced at all test concentrations. Swimming rate during feeding and total food strikes were reduced at ≥1.2 µg a.i.•L^{-1} and latency to first strike was significantly reduced at 2.5 µg a.i.•L^{-1} (Sandahl et al. 2005).

The long-term, non-lethal toxicity of chlorpyrifos to fish and other aquatic vertebrates has not been extensively studied. The lowest observed effects concentration (LOEC) for growth inhibition in juvenile fathead minnows decreased from 2.68 to 1.21 µg a.i.•L^{-1}, from 30 to 60 days exposure, respectively (Jarvinen et a*l*, 1983). Jarvinen and Tanner (1982) observed similar results, reporting a 32d-NOEC (embryo/larval growth) of >1.6 and <3.2 µg a.i.•L^{-1} for fathead minnows.
The larval metamorph was the most sensitive life stage reported for South African clawed frogs (*Xenopus laevis*) (96-h LC_{50} = 560 µg a.i.•L^{-1}), followed by the embryo (96-h LC_{50} = 2,410 µg a.i•L^{-1}), and the premetamorph life stages (96-h LC_{50} = 14,600 µg a.i.•L^{-1}) (Richards and Kendall 2002; El-Merhibi et al, 2004). A similar trend in life stage sensitivity was observed in 96-h EC_{50}s for malformations, with values of 240, 511, and 1,710 µg a.i.•L^{-1}reported for metamorphs, embryos, and premetamorphs, respectively (Richards and Kendall 2002; El-Merhibi et al, 2004).

Among invertebrate species, crustaceans and insect larvae are more sensitive to chlorpyrifos, and molluscs and rotifers are more tolerant (Giesy et al. 1999). Toxicity values for *Hyallela azteca* (amphipod) ranged from 0.04 to 0.138 µg a.i.•L^{-1}, representing decreasing toxicity with increasing age (Ankley and Collyard 1995; Phipps et al, 1995; Moore et al, 1998; EFED 2005).
The most sensitive water flea species reported in the literature were *Daphnia ambigua* and *Ceriodaphnia dubia*, with 48-h LC_{50}s of 0.035 and 0.05 µg a.i.•L^{-1}, respectively (Harmon et al., 2003; El-Merhibi *et al.*, 2004; Bailey *et al.*, 1997). *Daphnia magna* and *Daphnia pulex* were also sensitive to chlorpyrifos.(EFED 2005; Guilhermino et al. 2000; Gaizik et al, 2001).

Chironomus tentans was the most sensitive midge species with a range in 96-h EC_{50}s from 0.17 to 0.22 µg a.i.•L^{-1} for swimming behaviour, and a 96-h LC_{50} of 0.47 µg a.i.•L^{-1} (Lydy and Austin 2004; Schuler et al. 2005; Ankley and Collyard 1995).

Few studies are available on the long-term effects of chlorpyrifos to invertebrates. Ten-day LC_{50} values reported for invertebrate species were 0.07 µg a.i.•L^{-1} for *C. tentans* and *C. dubia* (Phipps et al, 1995; Ankley et al. 1994; Sherrard et al. 2002), 0.086 µg a.i.•L^{-1} for *H. azteca* (Phipps et al, 1985), and 0.17 µg a.i.•L^{-1} for *D. pulex* (van der Hoeven and Gerritsen 1997). The long-term value for *C. tentans* was lower than the short-term duration toxicity value (96-h LC_{50} = 0.47 µg a.i.•L^{-1}) (Ankley and Collyard 1995). The long-term toxicity value for *C. dubia*, 0.07 µg a.i.•L^{-1}, was slightly greater than the 48-h LC_{50} of 0.05 µg a.i•L^{-1} (El-Merhibi et al. 2004).

Laboratory studies have generally shown algae and aquatic plants to be tolerant of chlorpyrifos with EC_{50} values >100 µg a.i.•L^{-1} (Giesy et al. 1999). Long-term LC_{50}s ranged from 3.6 µg a.i.•L^{-1} (96-h) for the plankton *Diaptomis forbesi* (Thankamoni Amma and Kumar 1996), to >10,000 µg a.i.•L^{-1} (120-h) for the cyanobacterium *Synechoccocus leopoliensis* (Van Donk et al. 1992). Within this range are 96-h LC_{50} values of 140 µg a.i.•L^{-1} for the alga *Isochrysis galbana* and 150 µg a.i.•L^{-1} for the diatom *Thalassiosira* sp. (EFED 2005).

Marine Toxicity: Chlorpyrifos is relatively toxic to some marine fish, as seen from short-term toxicity data. For example, 96-h LC_{50} values are 0.4 and 0.58 µg a.i.•L^{-1} for 14-d old tidewater silverside (*Menidia peninsulae)* and striped bass (*Morone saxatilis*), respectively (Korn and Earnest 1974; Borthwick et al. 1985). For most species, static 96-h LC_{50} values are between 2 and 5 µg a.i.•L^{-1}, and flow-through 96-h LC_{50} values are between 0.5 and 4 µg a.i.•L^{-1} (Schimmel et al. 1983; Borthwick et al. 1985; Clark et al. 1985).

Long-term tests typically result in reduced weight and survivorship of fish fry exposed to chlorpyrifos. For example, 26-d exposure to 0.62 or 1.3 µg a.i.•L^{-1} chlorpyrifos reduced weight and survival, respectively, of California grunions (*Leuresthes tenuis)* fry (Goodman et al. 1985). Early life-stage tests also suggest that embryos are more tolerant to chlorpyrifos than fry.

Long-term toxicity data on marine invertebrates are limited to one study in which grass shrimp larvae receiving pulses of chlorpyrifos had a 25-d LC_{50} of 0.29 µg a.i.•L^{-1}. All larvae exposed to a single pulse of 1.6 µg a.i.•L^{-1} died (Key and Fulton 1993). Chlorpyrifos pulses, however, did not affect instar number, intermolt duration, developmental duration, or growth.

Information on the toxicity of chlorpyrifos to marine plants is limited to algae. Walsh (1983) reported 50 and 100% growth inhibition in the marine diatom *Skeletonema costatum* exposed to 1200 and 5000 µg a.i.•L^{-1}, respectively.

Water Quality Guideline Derivation: The short-term and long-term freshwater Canadian water quality guidelines (CWQGs) for chlorpyrifos for the protection of aquatic life were developed based on the CCME protocol (CCME 2007). The short-term guideline was developed using the statistical (Type A) approach. The long-term guideline was developed using the lowest-endpoint (Type B) approach. Marine toxicity data was not evaluated to see if there was sufficient data available to update the long-term marine water quality guideline for chlorpyrifos from 1997. No short-term marine water quality guideline was developed in 1997.

Short-term Freshwater Quality Guideline: Short-term exposure guidelines are derived using severe effects data (such as lethality) of defined short-term exposure periods (24 – 96-h). These guidelines identify estimators of severe effects to the aquatic ecosystem and are intended to give guidance on the impacts of severe, but transient, situations (e.g., spill events to aquatic receiving environments and infrequent releases of short-lived/nonpersistent substances). Short-term guidelines *do not* provide guidance on protective levels of a substance in the aquatic environment, as short-term guidelines are levels which *do not* protect against adverse effects.

Table 2. Endpoints used to determine the short-term CWQG for chlorpyrifos.

Species	Endpoint	Concentration (µg a.i.·L^{-1})
Fish		
L. macrochirus	96h LC_{50}	1.3
M. beryllina	96h LC_{50}	4.2
O. clarkii	96h LC_{50}	5.4
O. mykiss	96h LC_{50}	7.1
S.vitreum	48h LC_{50}	12.5*
L.cyanellus	36h LC_{50}	22.5
N.crysoleucas	36h LC_{50}	35
S. namaycush	96h LC_{50}	73
P. promelas	96h LC_{50}	140
G. affinis	36h LC_{50}	215
O. latipes	48h LC_{50}	250
I. punctatus	96h LC_{50}	280
Invertebrates		
H. azteca	96h LC_{50}	0.04
C. dubia	48h LC_{50}	0.05
S. vittatum	24h LC_{50}	0.06
G. lacustris	96h LC_{50}	0.11
C. tentans	96h EC_{50} (immobility)	0.193*
D. magna	48h EC_{50} (immobility)	0.412*
C. sabulosa	96h LC_{50}	0.57
A. aegypti	24h LC_{50}	7.1
P.californica	96h LC_{50}	10
Amphibians		
X. laevis	96h LC_{50}	511

*Value shown is the geometric mean of comparable values

The minimum data requirements for the Type A

Table 3. Short-term CWQG for Chlorpyrifos Resulting from the SSD Method.

	Concentration
SSD 5th percentile	0.023 µg a.i.•L^{-1}
SSD 5th percentile, LFL (5%)	0.009 µg a.i.•L^{-1}
SSD 5th percentile, UFL (95%)	0.048 µg a.i•L^{-1}

guideline approach were met, and a total of 22 data points were used in the derivation of the guideline. Toxicity studies meeting the requirements for primary and secondary data, according to CCME (2007) protocol, were considered in the derivation of the short-term species sensitivity distribution (SSD). Each species for which appropriate short-term toxicity was available was ranked according to sensitivity, and its centralized position on the SSD was determined using the Hazen plotting position (estimate of the cumulative probability of a data point). Intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive lifestage and endpoint. Table 2 presents the final dataset that was used to generate the fitted SSD for chlorpyrifos. Aquatic toxicity studies reported by the U.S. EPA (EFED, 2005) Environmental Fate and Effects Division (EFED) and Health Canada's Pesticide Management Regulatory Agency were classified as primary data, unless erroneous values or other factors raised concerns about data quality.

The log normal model provided the best fit of the twelve models tested (Figure 1). The equation of the fitted normal model is in the form of;

$$y = \frac{1}{2}\left[1 + 0.03268\left(\frac{x - 3.7666}{1.4898\sqrt{2}}\right)\right]$$

Where x is the log (concentration) and y is the proportion of species affected.

Summary statistics for the short-term SSD are presentated in Table 3. The concentration 0.023 µg a.i.•L^{-1}, is beyond the range of the data (to which the model was fit). Therefore, the 5^{th} percentile and its fiducial limits (FL) (boundaries within which a parameter is considered to be located) are extrapolations.

Therefore, the short-term CWQG value for protection of aquatic life in surface waters is 0.02 µg ai•L^{-1}.

Long-term Freshwater Quality Guideline: Long-term exposure guidelines identify benchmarks in the aquatic ecosystem that are intended to protect all forms of aquatic life for indefinite exposure periods.

Although the persistence of chlorpyrifos in water may be limited under field conditions by factors such as affinity for suspended solids and volatility in water, aquatic organisms may experience long-term exposure to the pesticide. Aquatic organisms may be chronically exposed to chlorpyrifos if they inhabit the waters receiving pesticide input from multiple sources, or multiple applications.

The acceptable long-term studies identified in this review consisted of one invertebrate species, two fish species, and two amphibian species. Based on the minimum data requirements; there were insufficient data to derive a long-term SSD for chlorpyrifos according to CCME (2007) protocol. There were also insufficient data to derive a long-term guideline using the lowest endpoint approach (Type B1). Therefore, following the tiered approach, the lowest endpoint approach (Type B2) guideline method was used to develop the long-term CWQG.

Under the Type B2 guideline method, for a nonphytotoxic substance such as chlorpyrifos, a guideline may be developed if the available primary and/or secondary studies include two fish species and two invertebrate species. Using the Type B2 guideline method to derive the long-term CWQG, the critical (lowest acceptable) endpoint was identified as a 96h-LC_{50} of 0.04 µg/L, for *Hyalella azteca* (Ankley and Collyard 1995). A safety factor of 20 was applied to the lowest data to derive the Type B2 guideline for chlorpyrifos.

Therefore, the long-term CWQG for the protection of freshwater life is 0.002 µg a.i.•L^{-1}.

Marine Water Quality Guideline: Marine toxicity data was not re-evaluated to see if there was sufficient data available to derive a short-term or long-term marine water quality guideline for chlorpyrifos. The marine guideline will be revisited in the future when it is believed there is enough data to update the guideline.

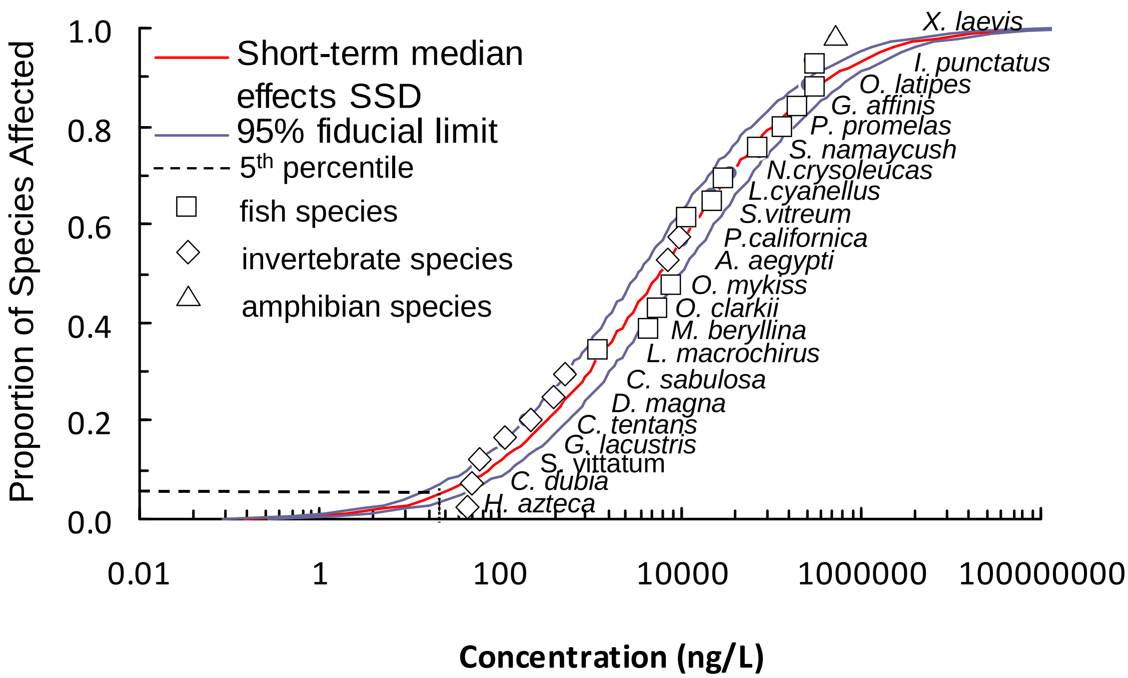

Figure 1. Short-term SSD representing the toxicity of chlorpyrifos in freshwater consisting of acceptable short-term LC50s of 22 aquatic species versus proportion of species affected.

The interim water quality guideline for chlorpyrifos for the protection of marine life is 0.002 µg a.i.•L^{-1} (CCME 1996). It was derived by dividing a 96-h LC_{50} of 0.04 µg a.i.•L^{-1} for mysid shrimp (Schimmel et al. 1983) by a safety factor of 20 (for nonpersistent substance, short-term toxicity study) (CCME 2007). This lowest short-term study, rather than the lowest long-term study, the 25-d LC_{50} of 0.29 µg a.i.•L^{-1} for grass shrimp larvae, was chosen for the guideline derivation because of the lower short-term threshold.

Therefore, the long-term CWQG for the protection of marine life is 0.002 µg a.i.•L^{-1}.

Considerations in Guideline Derivation: Based on a review of the literature, Giesy et al. (1999) proposed that providing protection to aquatic organisms from the effects of chlorpyrifos would also prevent effects in aquatic organisms from exposure to its transformation products. Although the activated form of chlorpyrifos, chlorpyrifos oxon, is a more effective inhibitor of AChE than the parent compound, the chlorpyrifos oxon is very sensitive to hydrolytic degradation, and thus occurs at low levels in the environment (Giesy *et al.*, 1999). Moreover, 3,5,6-trichloro-2-pyridinol (TCP), a primary metabolite of chlorpyrifos, does not inhibit AChE and is far less toxic to aquatic organisms than chlorpyrifos (Giesy *et al.*, 1999).

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