Canadian Water Quality Guidelines for the Protection of Aquatic Life

ENDOSULFAN

Endosulfan (CAS Registry Number 115-29-7) is a broad spectrum organochlorine insecticide. Pure grade endosulfan is a colourless crystalline solid whereas the technical grade product consists of crystalline flakes with a cream to brown colour and a faint odour of sulfur dioxide. Technical grade endosulfan is a mixture of the two biologically active isomers (α and β) in an approximate 2:1 to 7:3 ratio, in addition to impurities and degradation products (Mackay et al. 1997).

Endosulfan was first introduced in 1956. The current registrant of technical grade endosulfan in Canada is Bayer and Makteshim. As of 2007, endosulfan was banned in the European Union, the Philippines, Cambodia, and several other countries. In July, the European Commission proposed to add endosulfan to the list of chemicals banned under the Stockholm Convention on Persistent Organic Pollutants. If approved, all use and manufacture of endosulfan would be banned globally. Canada also announced that endosulfan is under consideration for phase-out.

Production and Uses: Endosulfan is produced by a Diels-Alder addition of hexachloro-cyclo-pentadiene and cis-butene-1,4-diol in xylene. The adduct is then hydrolysed to form the cis-diol or di-alcohol. The reaction of this cis-diol with thionyl chloride forms the final product (German Federal Environment Agency 2007).

Endosulfan is available as an emulsifiable concentrate, water dispersible powder, dispersion, dust or granules (IPCS 1988). It can be applied by dipping in a solution, high-pressure hand wand equipment or air blast equipment. All wettable powder formulations are to be packaged in water soluble bags (PMRA 2004).

It is registered in Canada to control a number of insect pests over a wide range of crops such as cucumber, tomato, lettuce, pepper apple, pear, apricot, cherry, plum, peach, grapes, bean, broccoli, brussel sprots, cabbage, celery, corn, potato, strawberry, and cauliflower.

Brimble et al. (2005) state that 22,025.96 kg of endosulfan were sold in Canada. On an annual basis, the data were primarily taken from one of the years 2001 to 2003 for each of the provinces and territories and then summed across all of the provinces and territories using the data from the most recent year of data collection. The most frequent data year was 2003. In addition, sales data may not fully depict pesticide use for residential applications.

Sources to the environment: In Canada, endosulfan is used in agricultural and residential applications. Direct application to soil, vegetation, trees and animals can result in exposure to non-target organisms.

In a set of interim mitigation measures taken in 2004 by PMRA to reduce possible contamination of aquatic environments, it is required that a ten metre vegetative buffer strip be maintained between all areas treated with endosulfan and sensitive freshwater habitats such as lakes, rivers, sloughs, ponds, coulees, prairie potholes, creeks, marshes, streams, reservoirs and wetlands, and estuarine/marine habitats. They also require a thirty metre buffer zone between the point of direct application and the closest downwind edge of sensitive freshwater habitats such as lakes, rivers, sloughs, ponds, coulees, prairie potholes, creeks, marshes, streams, reservoirs and wetlands, and estuarine/marine habitats. The application of endosulfan along with the possibility of accidental spillage, spray drift, leaching and runoff from terrestrial applications has the potential to expose aquatic biota to residues (PMRA 2004).

Table 1. Canadian Water Quality Guidelines (CWQG) for Endosulfan for the Protection of Aquatic Life (µg a.i.·L^{-1})

	Long-Term Exposure	Short-Term Exposure
Freshwater	0.003*	0.06**
Marine	0.002***	0.09**

* value calculated from acceptable long-term endpoints using the SSD approach
** value calculated from LC_{50} data using the SSD approach
*** value calculated from low-effect data using lowest endpoint approach

Fate, behaviour and partitioning: Endosulfan is a hydrophobic, nonpolar molecule. It has a low water solubility, with the α and β-isomers having a reported solubility in water of 0.32 and 0.33 mg·L^{-1}, respectively, at 20°C (Tomlin 2000). The melting point for technical

endosulfan has been reported as 70 -100°C (Mackay et al.1997).

The vapour pressure of 0.83 mPa at 20°C for technical endosulfan indicates that it has an intermediate to high volatility under field conditions (Tomlin 2000). The calculated Henry's law constants of 4.54×10^{-5} atm•m^3•mol^{-1} and 4.39×10^{-5} atm•m^3•mol^{-1} and the calculated 1/H values of 540 and 560, respectively, for the α and β-isomers indicate that both endosulfan isomers have the potential to volatilize from water or moist soil surfaces (Mackay et al. 1997). Endosulfan has a log K_{ow} value of 3.55 (Mackay et al. 1997), which indicates a potential for bioaccumulation in biota. Endosulfan is a non-ionic compound and thus will not dissociate at environmentally relevant pH (approximately pH 5.0 to pH 9.0).

In the environment, endosulfan can be transformed to a number of chemical products with endosulfan sulfate (CAS Number 1031-07-8) being the predominant product. Other products that have been identified are endosulfan diol, endosulfan hydroxycarboxylic acid and endosulfan lactone (German Federal Environment Agency 2004).

Endosulfan residues depurate rapidly in aquatic invertebrates and fish. Toledo and Jonsson (1992) reported depuration half-lives of 2.9 and 5.1 days for the α and β-isomers and 5.9 days for the endosulfan sulphate transformation product in zebra fish (*Brachydanio rerio*). Ernst (1977) reported a depuration half-life of 34 hours for the α-isomer in marine mussels (*Mytilus edulis*).

Analytical methods: One of the common determination methods for endosulfan involves the extraction from water using methylene chloride followed by gas chromatography combined with electron capture detection. In determining the residue levels, the sum of the α and β-isomers of endosulfan plus the endosulfan sulphate metabolite are to be considered. Detection limits are 0.015 μg a.i.•L^{-1} for α-endosulfan and, 0.024 μg a.i.•L^{-1} for β-endosulfan and 0.015 μg a.i.•L^{-1} for endosulfan sulfate (ATSDR 2000).

Lee et al. (1995) developed two enzyme immunoassays for the detection of endosulfan residues in water and soil. These optimized assays have detection limits of about 0.2 μg a.i.•L^{-1} and detect in the range of 0.2-10 μg a.i.•L^{-1}. These immunoassays detect endosulfan sulphate with a sensitivity similar to that for endosulfan but are four to ten times less sensitive to endosulfan diol.

You et al. (2004) utilized a gas chromatography method and an electron capture detector for the determination of endosulfan as well as other organochlorine pesticides in sediment. Four control sediments from different sources were spiked with a pesticide mixture and analysed for method validation. The method detection limits ranged from 0.22 to 0.85 μg a.i.•kg^{-1} dry sediment. Recoveries for the spiked samples (concentrations 1 to 400 μg a.i.•kg^{-1} dry sediment) were 71.9% to 129.8%.

Biological samples such as animal and plant tissues and milk normally require more extensive clean-up procedures such as column methods. Sensitivities from 0.2 to 10 μg a.i.•kg^{-1} were usual with most recoveries greater than 90% (Cheng and Braun 1977; Chopra and Mahfouz 1977; Frank et al. 1979; Zanini et al. 1980). Clean-up methods employing high-pressure liquid chromatography (HPLC) have been used and these methods reduce the time involved in the preparation of such samples (Demeter and Heyndrickx 1979). Detection limits for the α and β- isomers of endosulfan usually differ, the α-isomer being easiest to detect (Goebel et al. 1982). At low concentrations, the identification of endosulfan residues can be hampered by a variety of other pesticides or plant components. Endosulfan residues in environmental samples can only be considered valid if α and β-isomers together with endosulfan sulphate are found simultaneously.

Ambient concentrations: Endosulfan and its isomers were detected in sediment and water across Canada at low levels. Sediment concentrations of β-endosulfan ranged from <0.0029 to 0.0645 μg•g^{-1} in Ontario. Alpha endosulfan was detected in Ontario at limits of detection (LODs) in water between 12 and 20 μg•L^{-1} and β-endosulfan was detected at LODs between 10 and 60 μg•L^{-1}. In British Columbia, maximum concentrations reported in water were 0.021 μg•L^{-1} for α endosulfan, 0.0415 μg•L^{-1} for β-endosulfan and 0.312 μg•L^{-1} for endosulfan sulphate.

Mode of action: Endosulfan acts as a toxic chemical to a wide variety of insects and mites on contact through the blockage of GABA-(gamma amino butyric acid) gated chlorine channels. GABA is an inhibitory neurotransmitter in the central nervous system that operates through membrane hyperpolarization as mediated by increased chloride flux into nerve cells. By impairing the inhibitory actions of this complex, and,

thus, chloride influx into the nerve, hyper excitation results which, when prolonged, may lead to respiratory failure. External symptoms include depressed activity a few hours after exposure followed by hyper excitability, tremors and convulsions (Coats 1990). Convulsions can lead to death by interfering with pulmonary gas exchange and by generating severe metabolic acidosis (Coats 1990). Stimulation of the central nervous system, leading to convulsions, is the major characteristic of endosulfan toxicity (Ecobichon 1991).

Solvents and/or emulsifiers used with endosulfan in formulated products may influence its absorption into the system through all routes. Technical endosulfan is slowly and incompletely absorbed into the body whereas absorption is more rapid in the presence of alcohols, oils, and emulsifiers (Gupta and Gupta 1979).

***Freshwater Toxicity**:* In the following sections, all concentrations of endosulfan expressed in µg a.i.•L^{-1} refer to µg of active ingredient (a.i.) per litre. Toxicity test used in the development of the guideline are based on active ingredient, formulations in which the percent active ingredient were not sufficiently present (> 90% a.i.) were not used in the development of the guideline.

An extensive number of studies on short-term toxicity of fish have been conducted by industry and non-industrial research institutes. The tests include static, semi-static and flowthrough systems as well as a range of different test species. At the lower end of data LC_{50} values for fish are 0.10 µg a.i. •L^{-1} for the common carp (*Cyprinus carpio*) (Sunderam et al. 1992) and 0.20 µg a.i. •L^{-1} for the bony bream (*Nematolosa erebi*) (Sunderam et al. 1992). The snake-head catfish (*Channa punctata*) was the most tolerant fish species to endosulfan (96-h LC_{50} of 5780 µg a.i. •L^{-1}, Khillare and Wagh 1987).

For long-term toxicity to fish, no observed effect concentrations (NOECs) were reported in the range of 0.05 to0.4 µg a.i. •L^{-1}. A NOEC of 0.05 µg a.i. •L^{-1} was reported from a 21-day juvenile growth-test for rainbow trout (*Oncorhynchus mykiss*)(Knacker et al. 1991). A full life cycle exposure test (260 days) to fathead minnow (*Pimephales promelas*) (PMRA Monograph 2004) estimated a NOEC of 0.056 µg a.i. •L^{-1}. Several physiological, ethological and morphological effects of endosulfan have been reported in literature at concentrations ranging from 0.5 to 5 µg a.i. •L^{-1} (Joshi et al. 1980; Gill et al. 1991).

Aquatic invertebrates appear to be acutely susceptible to endosulfan concentrations in the order of 100 µg a.i. •L^{-1}, although considerable variation is evident, spanning several orders of magnitude. The lowest LC_{50} reported for a single species was the mayfly nymph (*Atalophlebia australis*) reported at 0.60 µg a.i. •L^{-1} (Leonard et al. 1999). The highest LC_{50} (15,000 µg a.i. •L^{-1}) reported was for the dragonfly nymph (*Pantala flavescens*) (Yadwad et al. 1990).

The lowest acceptable long-term endpoints (6-day MATC) reported were for the pink hydra (*Hydra vulgaris*) and green hydra (*Hydra viridissim*), reported at 0.06 and 0.07 µg ai. •L^{-1} respectively (Polino and Holdway 1999). The highest long-term endpoint (1,000 µg a.i. •L^{-1} for a 10-d EC_{50} changes in reproduction study) reported was for the rotifer (*Brachionus calyciflorus*) (Fernandez-Casalderrey et al. 1991).

Much less data are available on algae and plants in comparison to invertebrates and fishes. Green algae appear to be fairly tolerant to endosulfan. A 72-hour and 96-hour growth test for *Scenedesmus subspicatus* and *Pseudokirchneriella subcapitatum* resulted in EC_{50}s of 560 and 427.8 µg a.i. •L^{-1} respectively (PMRA Monograph 2004; DeLorenzo et al. 2002).

No acceptable toxicity studies on amphibians were found. However studies using formulated products indicate that amphibians may be sensitive to endosulfan (Gopal et al. 1981; Berrill et al. 1998; Harris et al. 2000b; Park et al. 2001). Because a formulated product was used, it is not possible to determine how much of the observed effects were due directly to endosulfan, as opposed to other chemicals present in the formulation. The toxicity of the formulation to amphibians appears to fall in a similar range as the toxicity of endosulfan to some of the more sensitive invertebrates and fish.

***Marine Toxicity**:* Short-term toxicity estimates for marine/estuarine fish ranged from 0.1 µg a.i. •L^{-1} to 0.38 µg a.i. •L^{-1}. Striped bass (*Morone saxatilis*) were the most sensitive (LC_{50} = 0.1 µg a.i. •L^{-1}) species tested.

At the time of this review, the only long-term toxicity endpoints for estuarine/marine fish consisted of a 28-d lowest observed effect concentrations (LOECs) for growth (0.6 µg a.i. •L^{-1}) and survival (1.3 µg a.i. •L^{-1})(US EPA, 1980).

Considerable variability was observed in toxicity estimates for estuarine/marine invertebrates exposed to technical grade endosulfan; each of the EC_{50} estimates of oysters differed by at least an order of magnitude.

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

Species	Endpoint	Concentration (µg a.i.·L^{-1})
Fish		
Cyprinus carpio	96-h LC_{50}	0.10
Nematolosa erebi	96-h LC_{50}	0.20
Morone saxatilis	96-h LC_{50}	0.22*
Macquaria ambigua	96-h LC_{50}	0.39*
Oncorhynchus mykiss	96-h LC_{50}	0.73*
Lepomis macrochirus	96-h LC_{50}	1.20*
Pimephales promelas	96-h LC_{50}	1.30*
Ictalurus punctatus	96-h LC_{50}	1.50
Gambusia affinis	96-h LC_{50}	2.30
Bidyanus bidyanus	96-h LC_{50}	2.35*
Melanotaenia duboulayi	96-h LC_{50}	3.11*
Anguilla anguilla	96-h LC_{50}	33.66*
Channa punctata	96-h LC_{50}	5780
Invertebrates		
Atalophlebia australis	72-h LC_{50}	0.60*
Cheumatopsyche sp.	48-h LC_{50}	0.85*
Jappa kutera	96-h LC_{50}	1.47
Pteronarcys californica	96-h LC_{50}	2.30
Gammarus fasciatus	96-h LC_{50}	5.80
Gammarus lacustris	96-h LC_{50}	6.00
Hyalella azteca	96-h LC_{50}	10.76*
Moinodaphnia macleayi	48-h LC_{50}	215
Daphnia magna	24-h LC_{50}	366.33*
Daphnia carinata	48-h LC_{50}	478
Ceriodaphnia dubia	48-h LC_{50}	491*
Procambarus clarkii	96-h LC_{50}	560*
Hydra viridissima	96-h LC_{50}	670
Biomphalaria tenagophila	96-h LC_{50}	852.93*
Brachionus calyciflorus	24-h LC_{50}	5150*
Oziotelphusa senex senex	96-h LC_{50}	5834.15*
Brachionus plicatilis	24-h LC_{50}	6600*
Pantala flavescens	24-h LC_{50}	15000
Amphibians		
Rana tigrina	96-h LC_{50}	1.80

*Value shown is the geometric mean of comparable values

Estimated EC_{50} values ranged from 0.45 µg a.i. •L^{-1} to 460 µg a.i. •L^{-1} and represented a difference of three orders of magnitude. Key et al. (2003) investigated the toxicity of endosulfan to selected life stages of the grass shrimp *Palaemonetes pugio* and found, over 96-hour exposures to endosulfan, that the adult grass shrimp (LC_{50} of 1.01 µg a.i. •L^{-1}) were more sensitive than the larvae (LC_{50} of 2.56 µg a.i. •L^{-1}). Embryonic grass shrimp exposed to endosulfan resulted in a LC_{50} of 117.0 µg a.i. •L^{-1} but with a large 95% confidence limit (0.73 to18,810 µg a.i. •L^{-1}). Low embryo toxicity could be partially explained by the presence of an embryonic coat which protects the embryo from potentially harmful conditions of the ambient water.

Long-term toxicity studies available for marine organisms consisted of a 28-d LC_{50} for the polychaete worm, *Nereis arenaceodentata*, which ranged between 80 to 145 µg a.i. •L^{-1} (Bishop et al.1983) and a 28-d NOEC for the mysid shrimp, *Mysidopsis bahia*, of 0.33 µg a.i. •L^{-1} (US EPA 1980).

Toxicity Modifying Factors: There are insufficient data regarding the effects of pH, temperature, hardness and UV radiation on the toxicity of endosulfan to reliably identify patterns of toxicity modifying effects or to normalize toxicity data.

Water Quality Guideline Derivation: The short-term and long-term Canadian Water Quality Guidelines (CWQGs) short-term and long-term exposures for endosulfan for the protection of aquatic life were developed based on the CCME protocol (CCME 2007). The short and long-term freshwater guideline, as well as the short-term marine guideline was developed using the statistical (Type A) approach with a Species Sensitivity Distribution (SSD). The long-term marine guideline was developed using the lowest-endpoint (Type B2) approach.

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 to 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 exposure guidelines *do not* provide guidance on protective levels of a substance in the aquatic environment, as short-term exposure guidelines are levels which *do not* protect against adverse effects, but

rather indicate the level where severe effects are likely to be observed.

The minimum data requirements for the Type A guideline approach were met, and a total of 33 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 endosulfan. For detailed information, including which studies were used to calculate the geomeans for the various species refer to Table 8.5 and 8.6 of the supporting document. 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 (PMRA) were classified as primary data, unless erroneous values or other factors raised concerns about data quality.

The log Fisher-Tippett model provided the best fit of the twelve models tested (Anderson-Darling Statistic (A^2) = 0.910). The equation of the fitted Fisher-Tippett model is of the form:

$$f(x) = e^{-e^{\frac{(L-x)}{s}}}$$

where *L* (3.4913) and *s* (1.5665), are the location and scale parameters of the model, x is the concentration metameter, and the functional response, f(x), is the proportion of taxa affected.

Summary statistics for the short-term SSD are presented in Table 3. The concentration 0.059 µg a.i.·L^{-1} , is outside the range of the data (to which the model was fit). Therefore the 5th percentile and its fiducial limits (FL) (boundaries within which a parameter is considered to be located) are extrapolations.

Therefore, the short-term exposure benchmark concentration indicating the potential for severe effects (e.g. lethality or immobilization) to sensitive freshwater life during transient events is 0.06 µg ai•L^{-1}.

Table 3. CWQG for short-term exposure for endosulfan in freshwater resulting from the SSD Method.

	Concentration
SSD 5th percentile	0.06 µg a.i.•L^{-1}
SSD 5th percentile, LFL (5%)	0.01 µg a.i.•L^{-1}
SSD 5th percentile, UFL (95%)	0.2 µg a.i•L^{-1}

Long-term Freshwater Quality Guideline: Long-term exposure guidelines identify benchmarks in the aquatic ecosystem that are intended to protect the most sensitive species and life stage for indefinite exposure periods. The minimum data requirements for the Type A guideline approach were met, and a total of 12 data points were used in the derivation of the guideline, however there is a desire for more ECx or EC10 data to improve the guideline. Toxicity studies meeting the requirements for primary and secondary data, according to CCME (2007) protocol, were considered in the derivation of the long-term SSD. Each species for which appropriate long-term toxicity was available was ranked according to sensitivity, and its centralized position on the SSD was determined using the Hazen plotting position. Intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive lifestage and endpoint. Table 4 presents the final dataset that was used to generate the fitted SSD for endosulfan. For detailed information, including which studies were using to calculate the geomeans for the various species refer to Table 8.8 of the supporting document. 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 (Anderson-Darling Statistic (A^2) = 0. 464). The equation of the fitted log normal model is of the form:

$$f(x) = \frac{1}{2}\left(1 + erf\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)\right)$$

where u (3.8089) and σ = 2.0219, are the location and scale parameters of the model, x is the concentration metameter, and the functional response, f(x), is the proportion of taxa affected and *erf* is the error function (a.k.a. the Gauss error function).

Summary statistics for the long-term SSD are presented in Table 5. The concentration 0.003 µg a.i.·L^{-1} , is beyond the range of the data (to which the model was fit). Therefore the 5th percentile and its fiducial limits are extrapolations.

Table 4. Endpoints used to determine the long-term freshwater CWQG for endosulfan.

Species	Endpoint	Concentration (µg a.i.·L^{-1})
Fish		
Oncorhynchus mykiss	21-d NOEC (growth)	0.05
Channa punctata	120-d LOEC ovarian steroidogenesis	0.24
Pimephales promelas	~ 1 year MATC (reduced survival and mean total length)	0.28
Invertebrates		
Hydra vulgaris	6-d MATC	0.06
Hydra viridissima	6-d MATC	0.07
Daphnia magna	21-d MATC reproduction	14.10*
Ceriodaphnia dubia	14-d MATC	14.10
Moinodaphnia macleayi	14-d MATC	28.30
Daphnia cephalata	14-d MATC (brood size)	113.14
Brachionus calyciflorus	10-d EC_{50} changes in reproduction	1,000*
Aquatic Plants and Algae		
Pseudokirchneriella subcapitatum	96-h EC_{50} growth rate	427.80
Scenedesmus subspicatus	72-h EC_{50}	560

*Value shown is the geometric mean of comparable values

Table 5. Long-term freshwater CWQG for endosulfan resulting from the SSD Method.

	Concentration
SSD 5th percentile	0.003 µg a.i.•L^{-1}
SSD 5th percentile, LFL (5%)	0.0007 µg a.i.•L^{-1}
SSD 5th percentile, UFL (95%)	0.01 µg a.i•L^{-1}

Therefore, the long-term exposure CWQG for the protection of freshwater life is 0.003 µg a.i.•L^{-1} for endosulfan.

Short-term Marine Water Quality Guideline: Short-term marine exposure guidelines are derived using severe effects data (such as lethality) of defined short-term exposure periods (24 to 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.

The minimum data requirements for the Type A guideline approach were met, and a total of 16 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 6 presents the final dataset that was used to generate the fitted SSD for endosulfan. For detailed information, including which studies were using to calculate the geomeans for the various species refer to Table 8.10 and 8.11 of the supporting document. 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 (PMRA) were classified as primary data, unless erroneous values or other factors raised concerns about data quality.

The log Fisher-Tippett model provided the best fit of the twelve models tested (Anderson-Darling Statistic (A^2) = 0. 374). The equation of the fitted Fisher-Tippett model is of the form:

$$f(x) = e^{-e^{\frac{(L-x)}{s}}}$$

where *L* (2.585) and *s* (0.584), are the location and scale parameters of the model, x is the concentration metameter, and the functional response, f(x), is the proportion of taxa affected.

Table 6. Endpoints used to determine the short-term marine CWQG for endosulfan.

Species	Endpoint	Concentration (µg a.i.·L^{-1})
Fish		
Morone saxatilis	48-h LC_{50}	0.1
Leiostomus xanthurus	48-h LC_{50}	0.232*
Lagodon rhomboides	48-h LC_{50}	0.3
Mugil cephlus	48-h LC_{50}	0.38
Mugil curema	48-h LC_{50}	0.6
Atherinops affinis	96-h LC_{50}	1.3
Cyprinodon variegatus	48-h LC_{50}	1.302*
Menidia beryllina	96-h LC_{50}	1.5
Invertebrates		
Penaeus duorarum	48-h LC_{50}	0.04
Acartia tonsa	48-h LC_{50}	0.144*
Crassostrea viginica	96-h LC_{50}	0.45
Mysidopsis bahia	48-h LC_{50}	0.692*
Palaemon puglo	48-h LC_{50}	1.31
Gammarus palustris	48-h LC_{50}	3.59*
Farfantepenaeus aztecus	48-h LC_{50}	35
Nereis arenaceodentata	96-h LC_{50}	730

*Value shown is the geometric mean of comparable values

Summary statistics for the short-term SSD are presented in Table 7. The concentration 0.104 µg a.i.·L^{-1} , is outside the range of the data (to which the model was fit). Therefore the 5th percentile and its fiducial limits (FL) (boundaries within which a parameter is considered to be located) are extrapolations.

Therefore, the short-term exposure benchmark concentration indicating the potential for severe effects (e.g. lethality or immobilization) to sensitive marine life during transient events is 0.09 µg a.i.•L^{-1} for endosulfan.

Table 7. Short-term marine life CWQG for endosulfan resulting from the SSD Method.

	Concentration
SSD 5th percentile	0.09 µg a.i.•L^{-1}
SSD 5th percentile, LFL (5%)	0.04 µg a.i.•L^{-1}
SSD 5th percentile, UFL (95%)	0.2 µg a.i.•L^{-1}

Long-term Marine Water Quality Guideline: The acceptable long-term studies identified for marine species consisted of only the mysid shrimp (*Mysidopsis bahia*), the polychaete worm (*Nereis arenaceodentata*), and the sheepshead minnow (*Cyprinodon variegates*). Based on minimum data requirements (CCME 2007), there were insufficient data available to derive a long-term marine guideline using the statistical approach (Type A) and 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 marine CWQG.

Using the Type B2 guideline method to derive the long-term CWQG, the critical endpoint was identified as a 48-h LC_{50} of 0.032 µg a.i.•L^{-1} for the copepod *Acartia tonsa* (Schimel 1980). A safety factor of 20 was applied to the lowest data to derive the long-term Type B2 guideline for endosulfan.

Therefore, the long-term exposure CWQG for the protection of marine life in surface waters is 0.0016 µg a.i.•L^{-1} for endosulfan.

Implementation and other considerations: The above guideline was developed using only toxicity data derived using the active ingredient. Formulated products which include endosulfan may be more or less toxic than the active ingredient. In regions of concern, additional sampling may be considered for known substances within fomulants to ensure aquatic life is not being impacted by other substances.

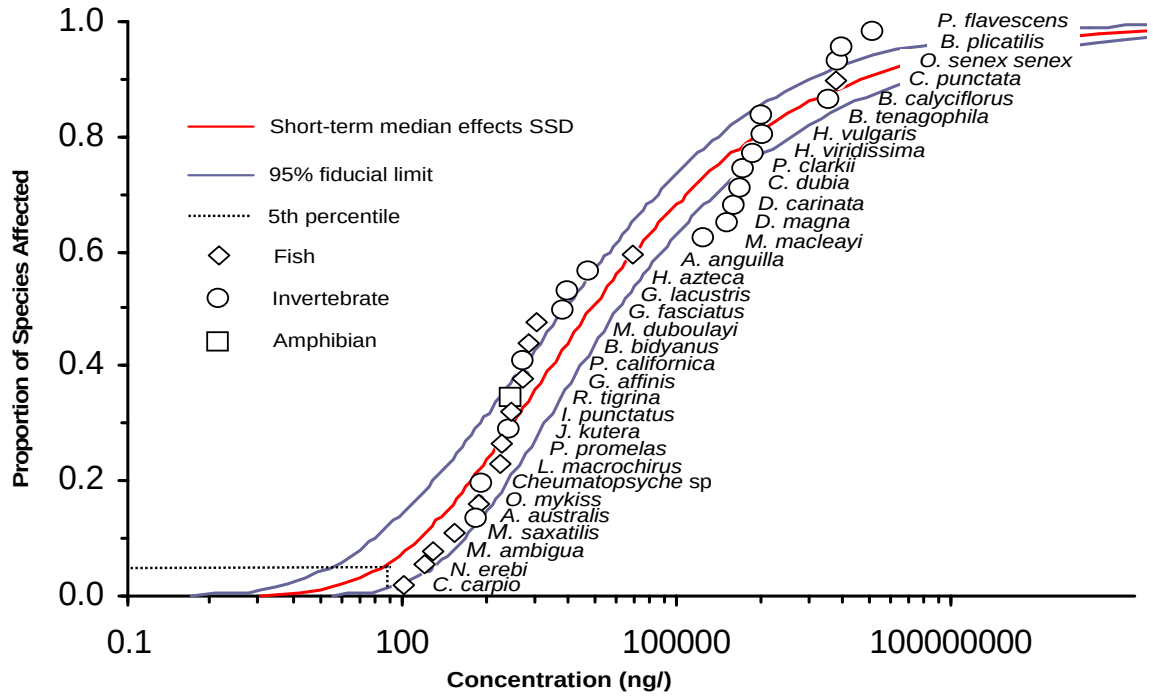

Figure 1. Short-term SSD representing the toxicity of endosulfan in freshwater consisting of acceptable short-term LC_{50}s of 33 aquatic species versus proportion of species affected.

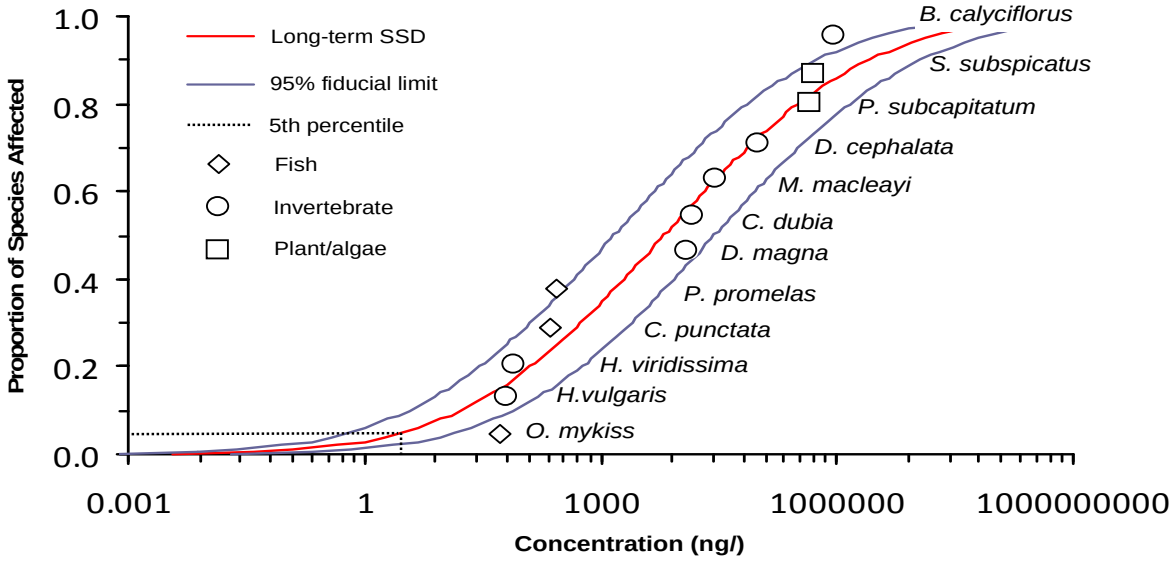

Figure 2. Long-term SSD representing the toxicity of endosulfan in freshwater consisting of acceptable long-term data endpoints of 12 aquatic species versus proportion of species affected.

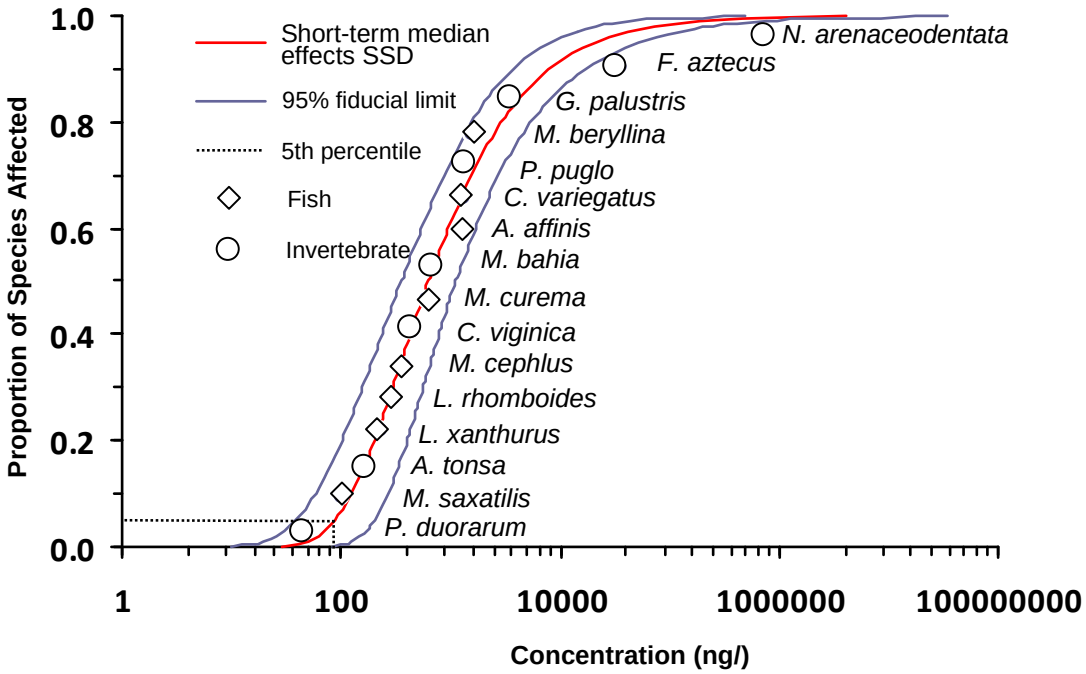

Figure 3. Short-term SSD representing the toxicity of endosulfan for marine organisms consisting of acceptable short-term LC_{50}s of aquatic species versus proportion of species affected.

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