Canadian Water Quality Guidelines for the Protection of Aquatic Life

GLYPHOSATE
2012

Glyphosate is a non-selective, post-emergence organophosphorus herbicide used to control annual and perennial grasses and broad leaved weeds (British Crop Protection Council 2000). The International Union of Pure and Applied Chemistry (IUPAC) chemical name of glyphosate is N-(phosphonomethyl) glycine and the CAS Registry Number is 1071-83-6. The chemical formula of glyphosate is $C_3H_8NO_5P$. Glyphosate is a white, odourless crystal with a molecular weight of 169.1 $g \cdot mol^{-1}$ (British Crop Protection Council 2000).

Glyphosate, for which the herbicidal activity was discovered in 1970, was first commercialized in 1974 by Monsanto and was registered in Canada in 1976 (Trotter et al. 1990; Franz et al. 1997). Since glyphosate commercialization, over 100 glyphosate-based formulations have been sold and used world-wide.

Uses: As a broad-spectrum, non-selective, systemic, and post-emergent herbicide, glyphosate targets essentially all annual and perennial plants (Franz et al. 1997). In croplands, glyphosate can, for example, be used to control acreage that is not in production, for minimum and no-tillage farming, on fence rows, in storage areas, along irrigation canals, and for pasture renovation. Glyphosate is also useful to remove ground vegetation from several plantations and fruit orchards as well as to remove deciduous trees, shrubs and vegetation from conifer forests.

Industrial applications of glyphosate include highways, roadsides, railroad rights-of-way, warehouses, storage areas, public waterways, golf courses, cemeteries and campus grounds. Finally, glyphosate can also have residential uses to eradicate poison ivy, poison oak, vines, and perennial weeds from patios, pavements, driveways, rockeries, and other locations (Franz et al. 1997).

Application rates are dependant on the different glyphosate-based formulations and type of use. The chemical is applied to the foliage, as no penetration will occur through bark. Recommended field application rates for controlling annual weeds range from 0.34 to 1.12 kg $a.i. \cdot ha^{-1}$ and for perennials from 1.12 to 4.48 kg $a.i. \cdot ha^{-1}$ (Weed Science Society of America, 1989).

Sources to the environment: Glyphosate may be introduced into the aquatic environment through spillage, accidental discharge, wind erosion of treated fields, or waste disposal during production, storage, and use. When applied according to the label instructions glyphosate rarely reaches water sources directly (Brønstad and Friestad 1985, Humphries et al., 2005). The low vapour pressure of glyphosate suggests that loss by evaporation is not likely to occur (Brønstad and Friestad 1985). Manufacturer labels strongly advise users not to apply any glyphosate-based formulation to a body of water. Therefore, entry into water can occur through accidental offsite movement of herbicide drift spray during application (Goldsborough and Beck 1989). Glyphosate is washed off plant foliage by rain, depending on the extent of the rainfall and the time since application of the herbicide (Brønstad and Friestad 1985).

Leachability of glyphosate is very low since it strongly binds to soil, and it is not sensitive to movement in runoff (Brønstad and Friestad 1985).

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

	Long-Term Exposure	Short-Term Exposure
Freshwater	800*	27,000**
Marine	NRG	NRG

* value calculated from no and low-effect data using the SSD approach
** value calculated from LC_{50} data using the SSD approach
NRG = no recommended guideline
Note: Some glyphosate formulations, including Roundup, currently contain a surfactant that may be considerably more toxic than glyphosate itself. This should be taken into consideration in any spill of this substance directly to surface water and in the evaluation of monitoring data.

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Fate, behaviour and partitioning: Glyphosate is highly soluble in water (11,600,000 µg a.i.·L^{-1}) and has a very low octanol-water partition coefficient (log K_{ow} = - 3.2 to -2.8). Nevertheless, once in the aquatic environment, glyphosate can rapidly dissipate, while it is stable for many years when dissolved in distilled water and kept at room temperature (Tooby 1985; Brønstad and Friestad 1985).

Glyphosate rapidly dissipates from water with half-lives ranging from a few days to several weeks (Tooby 1985; WHO 1994), with first-order half-lives in ponds ranging from 1.5 to 3.5 days (Goldsborough and Beck 1989, as cited in Franz et al. 1997). Dissipation rates of glyphosate from the water appear to be related to the water sediment content, water chemistry and photodegradation. Sediments are the major sink for glyphosate residue in water (Schuette 1998). Glyphosate has a very high organic carbon absorption coefficient (K_{oc} = 28,000 mL/g) which explains its strong reversible tendency to preferentially partition from water to sediments. In addition, glyphosate dissipation half-lives appear to be correlated with the water alkalinity, the longest half-lives being in water with the highest alkalinity (Goldsborough and Brown 1993). Photodegradation was initially thought to be a minor cause of glyphosate degradation (Rueppel et al. 1977) but additional evidence suggests that UV light photodegrades glyphosate. Reported photolytic half-lives at 100,000 µg a.i.·L^{-1} and 2,000,000 µg a.i.·L^{-1} were 4 days and 3 to 4 weeks, respectively (Lund-Hoie and Friestad 1986).

However, there are conflicting results concerning the adsorption of glyphosate onto suspended solids and benthic sediments in streams, with some studies indicating that more glyphosate remains in the water than others (Franz et al. 1997). Bowmer et al. (1986, as cited in Franz et al. 1997) claimed that at concentrations higher than 0.5 g a.i.·m^{-3}, suspended particles will remove less than 30% of the glyphosate from the water column.

In both aerobic and anaerobic conditions, (aminomethylphosphonic acid) AMPA is the principal metabolite produced from glyphosate degradation in water (Rueppel et al. 1977). The other metabolites represent less than one percent of the original total glyphosate.

Bioaccumulation of glyphosate in fish is not considered to be relevant (European Commission 2002), and is not expected to occur in aquatic organisms based on its low partition coefficient (Tooby 1985; Wang et al. 1994b).

The bioconcentration factor of Roundup, a glyphosate formulation, was reported to be 1.6 in bluegill sunfish (*Lepomis macrochirus*) (Tooby 1985). In carp (*Cyprinus carpio*) and tilapia (*Oreochromis mossambicus*), BCFs were calculated as 10.0 to 42.3 and 12.0 to 35.4 respectively (Wang et al. 1994a).

Analytical methods: Glyphosate is highly polar, water soluble and insoluble in organic solvents hence several approaches had to be developed to successfully analyze glyphosate in different matrices such as water, sediments, soil, vegetation and animal tissues (WHO 1994; Guo et al. 2005).

Several methods such as chromatography (gas chromatography (GC), high-performance liquid chromatography (HPLC), ion chromatography (IC)), enzyme-linked immunosorbent assays (ELISA), capillary electrophoresis (CE), and more, currently exist to detect glyphosate in different matrices (Stalikas and Konidari 2001).

Glyphosate analysis through GC requires an efficient chemical derivatization in order to make glyphosate less polar and sufficiently volatile to be chromatographed (Stalikas and Konidari 2001). Nevertheless, all GC-derived methods remained time-consuming and other approaches were subsequently proposed. Gas chromatography-mass spectrometry (GC-MS) methods have been successful in different matrices (Stalikas and Konidari 2001) with reported detection limits ranging from 0.01 to 0.2 µg a.i.·L^{-1} in water; 6 to 50 µg a.i.·kg^{-1} in soil; 50 µg a.i.·kg^{-1} for crops and 10 to 100 µg a.i.·kg^{-1} in various animal products (Alferness and Iwata 1994; Borjesson and Torstensson 2000; Royer et al. 2000).

Even given the great variety of available techniques to conduct glyphosate analysis, chromatographic methods remain the most popular (Stalikas and Konidari 2001).

Ambient concentrations: In 2004, a total of 203 surface water samples from 26 different field sites in Ontario were collected and analyzed for glyphosate and AMPA (Struger et al. 2008). Samples were taken between May and mid-December. Trace level detections for glyphosate were observed in 42 (21%) of the total samples analyzed in 2004. Overall mean glyphosate concentrations were typically in the low µg a.i.·L^{-1} range; typical maximum observed concentrations were in the 10–20 µg a.i.·L^{-1} range. The maximum glyphosate concentration observed was 41 µg a.i.·L^{-1}. Detectable residues occurred more frequently in spring and fall as compared to mid-summer. In 2005, as part

of the same study, a total of 299 surface water samples from 58 different sites were collected and analyzed for glyphosate and AMPA. Samples were taken between April and November. Trace level detections for glyphosate were observed in 45 (15%) of total samples analyzed. The maximum glyphosate concentration observed was 30.5 µg a.i.·L^{-1}. Trace level detections of AMPA were observed in 16 (5.4%) samples. Results were similar to 2004 in that typical mean glyphosate concentrations were in the low µg a.i.·L^{-1} range. Among these samples, maximum concentrations were typically in the 20–30 µg a.i.·L^{-1} range. The sample with the maximum AMPA concentration observed was 66 µg·L^{-1} (Struger et al. 2008).

From April to October 2007, a total of 739 surface water samples from over 150 sampling locations throughout Ontario were measured using ELISA. Concentrations exceeded the method detection limit of 0.1 µg a.i.·L^{-1} in 33% of the samples, with a maximum concentration of 12.0 µg a.i.·L^{-1} with peak concentrations occurring in late spring/early summer and fall (Byer et al. 2008).

A total of 853 samples were collected in Alberta from wetlands (Anderson et al. 2002), major rivers (Anderson 2005) and especially agricultural streams (Lorenz 2008) between 2002 and 2008, inclusive. Glyphosate was detected in 20% of the samples with 0.318 µg a.i.·L^{-1} and 13.832 µg a.i.·L^{-1} as median and highest concentrations on record, respectively.

The ministère du Développement durable, de l'Environnement et des Parcs in Québec monitors pesticides in agricultural regions of intense corn production. Since the program began in 1992, approximately 30 rivers have been sampled. The pesticides which were the most frequently detected (greater than 50% of water samples) were atrazine, metolachlor, bentazone, dicamba, 2,4-D, and dimethenamide (Giroux et al. 2006). On average glyphosate was detected in approximately 35% of samples between 2002-2004. AMPA was detected in approximately 5% of samples in the same time period. Glyphosate and AMPA were not analysed as part of this program prior to 2002. The maximum glyphosate concentration was measured in July 2003 at a concentration of 1.6 µg a.i.·L^{-1}.

Mode of action: Glyphosate is transported across the cuticle of the plant, most likely due to diffusion (Caseley and Coupland 1985), with the concentration gradient of glyphosate between the amount deposited on the cuticle and the amount already within the plant having an effect on the rate of uptake (Franz et al. 1997). After being taken up, glyphosate is rapidly translocated in most plants, undergoing transport between cells, within cell walls, and in xylem tissues, which is likely the reason for its effectiveness as a systemic herbicide (Franz et al. 1997). Glyphosate can penetrate cell walls, allowing it to enter the symplast and be translocated throughout the plant through the phloem (Franz et al. 1997). As described, long-range transport of glyphosate within plants occurs, and glyphosate can also undergo short-range transport on a cell by cell basis, via the plasmodesmata (Franz et al. 1997). Glyphosate is translocated within plants to active sinks over extended periods of time (Franz et al. 1997), and tends to accumulate in the meristematic regions (Sprankle et al. 1975; Gougler and Geiger 1981; Foley et al. 1983).

The exact target of glyphosate within the plant has been described; glyphosate inhibits 5-enolpyruvoylshikimate 3-phosphate (EPSP) synthase which is a vital enzyme in aromatic amino acid biosynthesis (Franz et al. 1997). EPSP catalyzes the formation of EPSP from phosphoenolpyruvate (PEP) and shikimate 3-phosphate (S3P). This is the vital step in producing chorismate, which is required for the biosynthesis of essential aromatic amino acids, tetrahydrofolate, ubiquinone, and vitamin K which are all very important products (Carlisle and Trevors 1988; Franz et al. 1997). This pathway is present only in plants and photosynthetic microorganisms (Franz et al. 1997), which is likely the reason for its low toxicity to other groups of organisms. No other commercial herbicide family works in the same manner as glyphosate, and attempts to reproduce the specificity of glyphosate are not as effective (Franz et al. 1997).

Results of glyphosate toxicity in plants include foliar chlorosis followed by necrosis, with other signs such as leaf wrinkling or malformation also present (Franz et al. 1997). A gradual wilting as well as a yellowing and/or browning of the plant may also occur (Schuette 1998). Effects of glyphosate on plants can be seen as early as 2 to 4 days after exposure, though they may not be visible for up to a week, depending on weather (Schuette 1998). The death of the plant can take anywhere from several days to weeks (Franz et al. 1997).

No studies were available that looked at the mode of action of glyphosate in fish, aquatic invertebrates, or amphibians.

Freshwater Toxicity: Results of short-term toxicity tests on a wide variety of species (including mammals)

indicates glyphosate is relatively non-toxic (Atkinson 1985).

Glyphosate has been determined to be relatively non-toxic to fish species. Bluegill sunfish (*Lepomis macrochirus*), for example, have 24-h LC_{50}s ranging from 150,000 to 240,000 µg a.i.·L^{-1}, and 96-h LC_{50}s ranging from 2400 to >1 000 000 µg a.i.·L^{-1} (Folmar et al. 1979; Mayer and Ellersieck 1986; US EPA 2007 a; b; c).

The short-term toxicity of glyphosate to the common carp (*Cyprinus carpio*) was examined by Ramaprabhu et al. (1991), who reported 24-h LC_{50}s of 6,000 and 10,000 µg a.i.·L^{-1}. The fathead minnow (*Pimephales promelas*) is less sensitive, with reported 24-h LC_{50} values of 84,900 to 97,000 µg a.i.·L^{-1} (Folmar et al. 1979; Mayer and Ellersieck 1986; US EPA 2007b), and 96-h LC_{50}s of 9,400-97,000 µg a.i.·L^{-1} (Folmar et al. 1979; Mayer and Ellersieck 1986; US EPA 2007 b; c).

Rainbow trout (*Oncorhynchus mykiss*) was found to be the most extensively studied species, with the greatest number of endpoints reported. These values, almost all LC_{50}s, have a wide range, as shown by the values at 24-h ranging from 21,000-240,000 µg a.i.·L^{-1} (Folmar et al. 1979; Mayer and Ellersieck 1986; Wan et al. 1989) and a range of 8200 to >1,000,000 µg a.i.·L^{-1} at 96-h (Folmar et al. 1979; Mayer and Ellersieck 1986; Wan et al. 1989; US EPA 2007 a; b; c). A 96-h LOEC for rainbow trout was reported as 8700 µg a.i.·L^{-1} (US EPA 2007b).

The limited information available on the long-term effects of glyphosate on freshwater fish indicates that fish are not very sensitive to long-term glyphosate toxicity. Fathead minnows have a reported 255-d LOEC of 25,780 µg a.i.·L^{-1} (OPP Pesticides Database 2007), which was the most sensitive long-term endpoint found for fish. Early life stage Coho salmon (*Oncorhynchus kisutch*) had a reported 21-d NOEC of 130,000 µg a.i.·L^{-1}, which was similar to the 7-d NOEC of 150,000 µg a.i.·L^{-1} based on hatching success of rainbow trout (Graham van Aggelen (Environment Canada) pers. comm. 2007).

Invertebrates were not very sensitive to short-term glyphosate toxicity. *Daphnia magna* was the most studied species, and the most sensitive, with 4-h LC/EC_{50}s for mortality/immobilization ranging from 3000 to >1,000,000 µg a.i.·L^{-1} (US EPA 2007a; b; c). The midge *Chironomus plumosus* had reported 48-h LC/EC_{50}s of 13,000 to 55,000 µg a.i.·L^{-1} (Folmar et al. 1979; US EPA 2007b; c). *Daphnia pulex* had similar sensitivities to glyphosate toxicity as *Daphnia magna*, with 48h LC/EC_{50}s ranging from 7 900-242 000 µg/L (US EPA 2007b).

Very insensitive species of invertebrates included *Gammarus pseudolimnaeus*, with 48-h LC_{50}s of 42,000 and 62,000 µg a.i.·L^{-1} (US EPA 2007b) and *Mysidopsis bahia* (mysid shrimp) with a 96-h LC_{50} of 40,000 µg a.i.·L^{-1} (US EPA 2007a).

The USEPA Restricted database (2007c) reported 21-d LOECs of 2,100 and 96,000 µg a.i.·L^{-1} and NOELs of 1,200 and 50,000 µg a.i.·L^{-1} for *Daphnia magna*. *Hyalella azteca* toxicity was reported by James Elphick (Summit Environmental Consultants Ltd. 2007), indicating a 14-d EC_{10} of 53,900 µg a.i.·L^{-1} for survival and an IC_{10} for dry weight of 20,500 µg a.i.·L^{-1}, putting it closer to the range of *C. dubia* and very insensitive to glyphosate toxicity. The snail *Pseudosuccinea columella* was tested for hatching success after 12 days of exposure, resulting in a LOEC/L of 10,000 µg a.i.·L^{-1} and a NOEC/L of 1000 µg a.i.·L^{-1} (Tate et al. 1997).

Freshwater plants and algae are not very sensitive to short-term glyphosate toxicity. Cedergreen and Streibig (2005) tested the growth rate of *Pseudokirchneriella subcapitata* after 24-h, reporting an EC_{50} of 270,000 µg a.i.·L^{-1} and an EC_{10} of 92,500 µg a.i.·L^{-1}. Duckweed (*Lemna minor*) was the most sensitive algae or aquatic plant species found, with reported 48-h EC_{50}s (population) of >16,910 µg a.i.·L^{-1} and 2,000 µg a.i.·L^{-1} (OPP Database 2007).

Freshwater algae and aquatic plants are generally more sensitive to long-term glyphosate toxicity than invertebrates and fish overall, however they are still relatively insensitive to glyphosate toxicity. The blue-green algae *Anabaena flosaquae* had a reported 5-d NOEL of 12,000 µg a.i.·L^{-1} (US EPA 2007c), though the green algae *Chlorella pyrenoidosa* and *Chlorella vulgaris* had 96-h EC_{50}s for growth inhibition of 3530 and 4696 µg a.i.·L^{-1} respectively (Ma et al. 2001; 2002). *Lemna gibba* was even more sensitive, with reported 14-d NOELs of 1400 and 1800 µg a.i.·L^{-1} (US EPA 2007c).

Short-term toxicity of glyphosate to freshwater amphibians has been reported in a few species. In the Australian frog *Crinia insignifera*, the 96-h LC_{50} has been reported as 78,000 µg a.i.·L^{-1} (US EPA 2007a; b). The amphibian *Litoria moorei* has reported 96-h LC_{50}s of 11,600 and 110,800 µg a.i.·L^{-1} (US EPA 2007a). Green frogs (*Rana clamitans*) have reported 24 and 96-h LC_{50}s of >38 900 µg a.i.·L^{-1} (Howe et al. 2004). Several

recent studies conducted on amphibians have shown that amphibians are one of the most sensitive vertebrate groups to the toxicological effects of glyphosate. The LC_{50} for many amphibians is between 10,000 and 1000 $\mu g \cdot L^{-1}$ (Govindarajulu 2008), however many of these studies are based on toxicity tests using formulated glyphosate products which were not considered in the development of the glyphosate guideline. Formulated studies are typically not used in the development of a guideline due to the fact that pesticides are typically detected by looking for the active ingredient in the environment and that there are normally several formulations for each active ingredient in use.

Marine Toxicity: No acceptable marine toxicity studies of glyphosate toxicity were found.

Water Quality Guideline Derivation: The short-term and long-term freshwater Canadian water quality guidelines (CWQGs) for glyphosate for the protection of aquatic life were developed based on the CCME protocol (CCME 2007). The short-term and the long-term guidelines were developed using the statistical (Type A) approach. Due to a lack of data, no marine water quality guidelines for glyphosate were derived.

Short-term Freshwater Benchmark Concentration: Short-term benchmark concentrations 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 19 data points were used in the derivation of the guideline. Toxicity studies meeting the requirements for primary and secondary data, according to the 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. For this reason, some of the studies listed below may appear higher than concentrations reported in the previous section. Table 2 presents the final dataset that was used to generate the fitted SSD for glyphosate. 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.

Table 2. Endpoints used to determine the short-term CWQG for glyphosate (for full species names please refer to CCME 2012).

Species	Endpoint	Concentration (μg a.i.$\cdot L^{-1}$)
Fish		
I. punctatus	96h LC_{50}	30,015*
L. macrochirus	96h LC_{50}	67,368*
O. gorbuscha	96h LC_{50}	56,711*
O. keta	96h LC_{50}	42,372*
O. kisutch	96h LC_{50}	73,206*
O. mykiss	96h LC_{50}	68,480*
O. tshawytscha	96h LC_{50}	66,747*
P. promelas	96h LC_{50}	56,632*
Invertebrates		
C. dubia	48h LC_{50}	147,000
C. plumosus	48h LC_{50}	23,434*
D. magna	48h LC_{50}	114,709*
D. pulex	48h LC_{50}	43,724*
G. pseudolimnaeus	48h LC_{50}	51,029*
H. azteca	96h LC_{50}	144,603*
Amphibians		
C. insignifera	96h LC_{50}	55,647*
L. moorei	96h LC_{50}	29,018*
R. clamitans	96h LC_{50}	38,900
Aquatic Plants and Algae		
C. fusca	24h Reproduction	377,000
P. subcapitata	24h EC_{50} (growth)	270,000

*Value shown is the geometric mean of comparable values

The log Fisher-Tippett model provided the best fit (Anderson-Darling Statistic (A^2) = 0.247) of the twelve models tested (Figure 1). The equation of the fitted Fisher-Tippett model is of the form:

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

where *L* (4.6914) and *s* (0.23677), 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.

The short-term SSD is shown in Figure 1 and summary statistics are presented in Table 3. The concentration 27,000 µg a.i.·L^{-1}, is within 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 interpolations.

Table 3. Short-term CWQG for Glyphosate resulting from the SSD Method.

	Concentration
SSD 5th percentile	27,000 µg a.i.•L^{-1}
SSD 5th percentile, LFL (5%)	24,000 µg a.i.•L^{-1}
SSD 5th percentile, UFL (95%)	30,500 µg a.i•L^{-1}

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 27,000 µg ai•L^{-1} for glyphosate

Long-term Freshwater CWQG: Long-term exposure guidelines identify benchmarks in the aquatic ecosystem that are intended to protect all forms of aquatic life for indefinite exposure periods. The minimum data requirements for the Type A guideline approach were met, and a total of 18 data points were used in the derivation of the guideline, however there is a desire for more EC_x or EC_{10} 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 species sensitivity distribution (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. For this reason, some of the studies listed below may appear higher than concentrations reported in the previous section. Table 4 presents the final dataset that was used to generate the fitted SSD for glyphosate. Aquatic toxicity studies

Table 4. Endpoints used to determine the long-term CWQG for glyphosate (for full species names please refer to CCME 2012).

Species	Endpoint	Concentration (µg a.i.·L^{-1})
Fish		
O. kisutch	21d ELS NOEC	130,000
O. mykiss	7d NOEC (hatching)	150,000
P. promelas	255d NOEC	25,700
Invertebrates		
C. dubia	7d NOEC (Mortality)	65,000
D. magna	21d MATC	10,487*
H. azteca	14d IC_{10} (dry weight)	20,500
P. columella	12d MATC (hatching)	3162*
Aquatic Plants and Algae		
A. flosaquae	5d NOEL	12,000
C. pyrenoidosa	96h EC_{50} (growth inhibition)	3530
C. vulgaris	96h EC_{50} (growth inhibition)	4696
L. gibba	14d NOEL	1587*
M. sibiricum	14d IC_{50} (growth)	1474
N. pelliculosa	5d NOEL	1800
P. pectinatus	28d MATC (growth)	3162*
P. subcapitata	5d NOEL	10,000
S. acutus	96h MATC (Population changes)	2820*
S. obliquus	96h EC_{50} (growth inhibition)	55,858
S. quadricauda	96h MATC (Population changes)	1090*

*Value shown is the geometric mean of comparable values

reported by the U.S. EPA (EFED 2005) Environmental Fate and Effects Division 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 Fisher-Tippett model provided the best fit (Anderson-Darling Statistic (A^2) = 0.284) of the twelve models tested (Figure 2). The equation of the fitted Fisher-Tippett model is of the form:

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

where *L* (3.5994) and *s* (0.6334), 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.

The long-term SSD is shown in Figure 2 and summary statistics are presented in Table 5. The concentration 800 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.

Therefore, the long-term CWQG for the protection of freshwater life is 800 µg a.i.•L^{-1} for glyphosate

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

	Concentration
SSD 5th percentile	800 µg a.i.•L^{-1}
SSD 5th percentile, LFL (5%)	490 µg a.i.•L^{-1}
SSD 5th percentile, UFL (95%)	1320 µg a.i•L^{-1}

***Marine CWQG*:** No Marine data were found for glyphosate, the marine guideline will be revisited in the future when it is believed there are enough data to develop a marine guideline.

Considerations in Guideline Derivation: Although water quality parameters such as hardness and pH have been examined as possible glyphosate toxicity modifying factors, there is no conclusive evidence that these affect toxicity of glyphosate.

The isopropylamine salt and commercial Roundup product have often been shown to be more toxic than the active ingredient (glyphosate). The previous CWQG was based on toxicity tests using the Roundup formulation. According to current practice, CWQGs are based only on the active ingredient. The surfactant (polyethoxylated tallow amine or POEA or MON 0818) rather than the active ingredient in these formulations has been shown to be responsible for much of the toxic effects to aquatic life.

Aminomethylphosphonic acid (AMPA) is the dominant and possibly the only conversion product of glyphosate (Brønstad and Friestad 1985). Rueppel et al. (1977) have indicated that AMPA is like other, naturally occurring aminomethlyphosphonates, and may be used as a source of phosphorus by certain organisms. As AMPA is similar to a naturally occurring substance used by organisms in the environment, it is unlikely that it reaches levels that would constitute a threat to the environment (Brønstad and Friestad 1985).

Implementation considerations: This CWQG is based only on toxicity data for the active ingredient. The previous CWQG was based on Roundup which also contains the surfactant described above. Roundup is not registered for direct application to water. Alternative formulations that do not use this surfactant are now available in some parts of the world (but not in Canada) and these formulations have much lower toxicity to some non-target organisms (Govindarajulu 2008).

Monitoring for glyphosate alone could underestimate risk to aquatic organisms as a result of the spill of a formulated product containing POEA. In addition POEA is a component of some non-glyphosate pesticides. To address this issue, CCME is considering developing a CWQG for POEA.

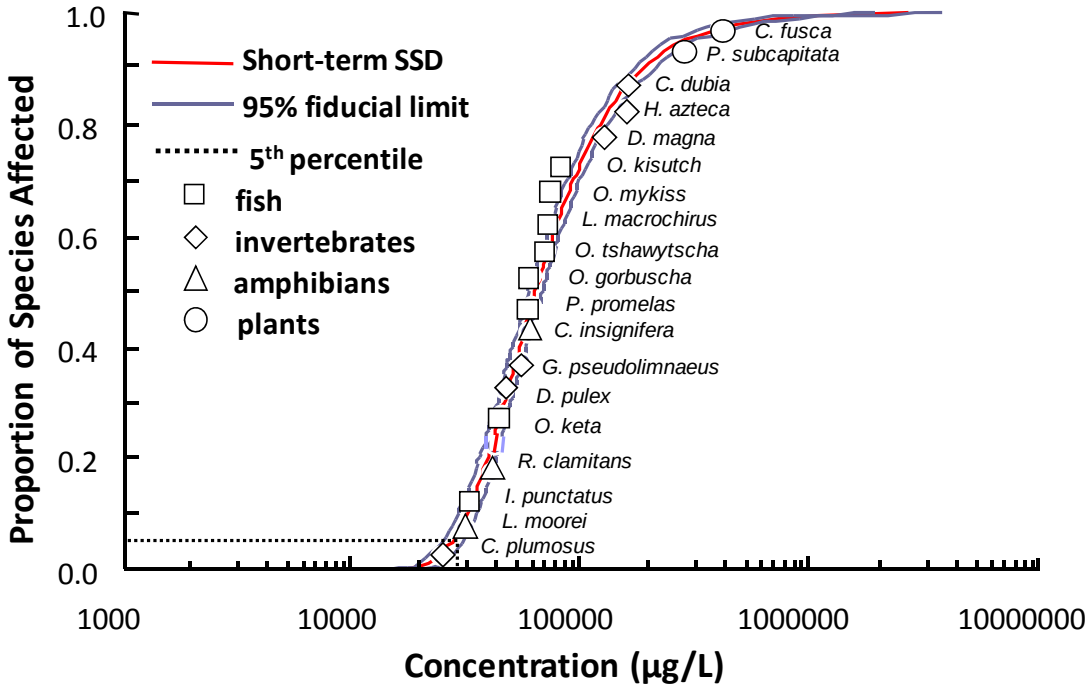

Figure 1. Short-term benchmark representing the toxicity of glyphosate in fresh water consisting of acceptable short-term LC_{50}s of 19 aquatic species versus proportion of species affected.

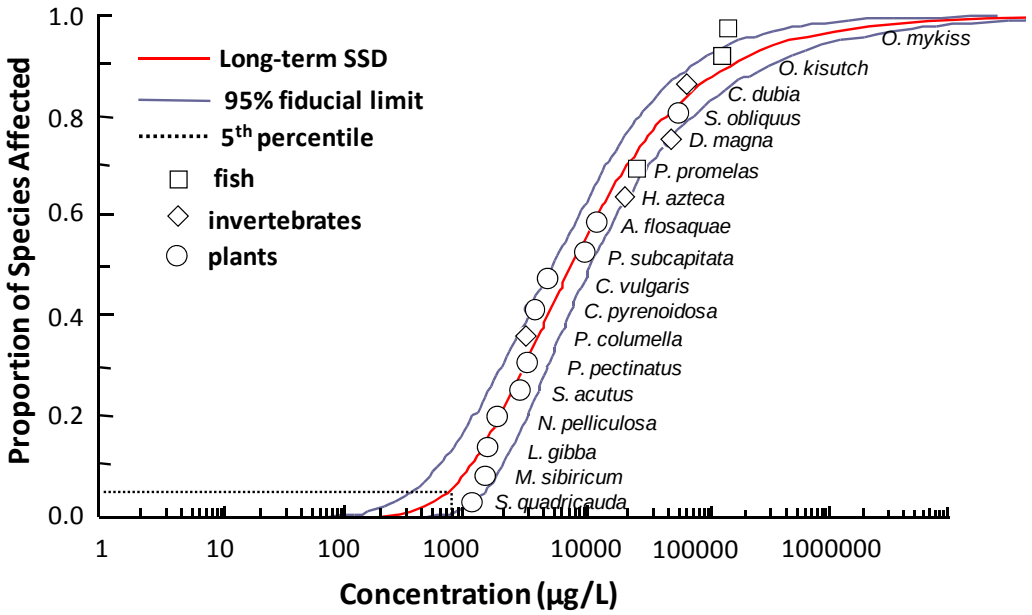

Figure 2. Long-term SSD representing the toxicity of glyphosate in fresh water consisting of acceptable long-term data endpoints of 18 aquatic species versus proportion of species affected.

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