Scientific Criteria Document for the Development of the Canadian Water Quality Guidelines for the Protection of Aquatic Life

GLYPHOSATE

PN 1469

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NOTE TO READERS

The Canadian Council of Ministers of the Environment (CCME) is the primary minister-led intergovernmental forum for collective action on environmental issues of national and international concern.

This document provides the background information and rationale for the development of the Canadian Water Quality Guidelines for glyphosate. For additional scientific information regarding these water quality guidelines, please contact:

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These guidelines are included as updates in the *Canadian Environmental Quality Guidelines*, which was published by CCME in October of 1999. The Canadian Environmental Quality Guidelines are available online at http://ceqg-rcqe.ccme.ca/.

This scientific supporting document is available in English only. Ce document scientifique du soutien n'est disponible qu'en anglais avec un résumé en français.

Reference listing:

CCME. 2012. Canadian Water Quality Guidelines : Glyphosate. Scientific Criteria Document. Canadian Council of Ministers of the Environment, Winnipeg.

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SCIENTIFIC CRITERIA DOCUMENT - CANADIAN WATER QUALITY GUIDELINES FOR THE PROTECTION OF AQUATIC LIFE FOR GLYPHOSATE

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LIST OF ACRONYMS

a.i.	Active ingredient
ACR	Acute-Chronic Ratio
BCF	Bioconcentration Factor
BMP	Beneficial management Practice
CAS	Chemical Abstract Services
CBI	Confidential Business Information
CCME	Canadian Council of Ministers of the Environment
CDF	Cumulative Distribution Function
CE	Capillary electrophoresis
CEI	Cantox Environmental Inc.
ChV	Chronic value
d	day
EC	Environment Canada
EC_X	Effects concentration affecting X percent of the population
ELISA	Enzyme-linked immunosorbent assay
ELS	Early Life Stage
EPS	Environmental performance standards
EQS	Environmental Quality Standard
ERL	Environmental risk limit
FPT	Federal-Provincial-Territorial
GC	Gas chromatography
GMAV	Genus Mean Acute Value

EXECUTIVE SUMMARY

This report describes the development of Canadian Water Quality Guidelines (CWQG) for the protection of freshwater aquatic life for the active ingredient glyphosate. Glyphosate, IUPAC chemical name of N-(phosphonomethyl) glycine (CAS Registry Number 1071-83-6) is a non-selective, post-emergence organophosphorus herbicide.

Glyphosate is highly polar, water soluble, and insoluble in organic solvents hence several approaches to residual analysis had to be developed to successfully analyze glyphosate in different matrices. Several methods such as chromatography (gas chromatography (GC), high-performance liquid chromatography (HPLC), ion chromatography (IC)), enzyme-linked immunosorbent assays (ELISA), and capillary electrophoresis (CE) exist to detect glyphosate in different matrices. HPLC is a preferred approach in the analysis of glyphosate from water samples with detection limits ranging from 6 to 50 µg/L in water.

Glyphosate is used in several forms (not to be confused with formulations) to enhance absorption into the plants. The glyphosate parent compound molecule is a weak organic acid that can be used in various salt forms such as the isopropylamine, the trimethylsulfonium and the diammonium salts. Toxicity data for all glyphosate forms were pooled in order to obtain the standard values as there is currently not enough evidence to demonstrate that the toxicity among the different salts differs and because the term glyphosate has generally been used to indicate all forms.

Glyphosate has been determined to be relatively non-toxic to aquatic life. The short and long-term freshwater CWQG for glyphosate for the protection of aquatic life were developed based on the CCME protocol (CCME 2007). The short-term CWQG was developed using the statistical or Type A approach, as sufficient data was available. The long-term CWQG was developed using the statistical (Type A approach), as sufficient data was available. SSDs were developed using the log-Fisher-Tippett model for both short-term and for long-term data. The short-term benchmark concentration and long-term CWQG for glyphosate were 27,000 and 800 µg a.i./L, respectively. It should be noted that some formulations of pesticides containing glyphosate incorporate surfactants which are more toxic than the active ingredient. It is recommended that guidelines be developed for these surfactants or that site specific guidelines be used in areas where this may be of concern.

Guideline	**Value (µg a.i./L)**
Short-term Freshwater	27,000*
Long-term Freshwater	800**
Short-term Marine	NRG
Long-term Marine	NRG

* value calculated from LC_{50} data using the SSD approach

** value calculated from no and low-effect data using the SSD approach

NRG = no recommended guideline

Note: Some glyphosate formulations, specifically Roundup, currently contain a surfactant that is considerably more toxic than glyphosate alone. This should be taken into consideration in any spill of this substance directly to surface water.

RÉSUMÉ

Le présent rapport décrit le processus d'élaboration des Recommandations canadiennes pour la qualité des eaux (RCQE) en vue de la protection de la vie aquatique en eau douce relativement à la matière active glyphosate. Le glyphosate est un herbicide organophosphoré non sélectif de postlevée dont le nom chimique est le N-(phosphonométhyl)glycine. Selon la nomenclature de l'Union internationale de chimie pure et appliquée (UICPA), son numéro CAS est le 1071-83-6.

Le glyphosate est un composé très polaire qui est soluble dans l'eau, mais insoluble dans les solvants organiques. Plusieurs approches ont du être élaborées pour analyser le glyphosate dans les différents milieux : chromatographie en phase gazeuse, chromatographie liquide à haute performance, chromatographie ionique, essais immunoenzymatiques ELISA et électrophorèse capillaire. La chromatographie liquide à haute performance représente la méthode privilégiée pour doser le glyphosate dans les échantillons d'eau; les limites de détection de cette méthode varient de 6 à 50 µg/L d'eau.

Le glyphosate est utilisé sous différentes formes (à ne pas confondre avec des formulations) pour accroître son absorption par les végétaux. Le glyphosate est un acide organique faible qui peut être utilisé sous la forme de divers sels, par exemple: les sels d'isopropylamine, les sels de triméthylsulfonium et les sels de diammonium. Les données de toxicité pour toutes les formes de glyphosate ont été regroupées afin d'obtenir les valeurs standard puisque selon les données actuellement disponibles, il n'existe pas de preuves suffisantes pour démontrer que la toxicité des différents sels de glyphosate diffère. De plus, le terme « glyphosate » désigne généralement toutes les formes de glyphosate.

Il a été déterminé que le glyphosate est relativement non toxique pour la vie aquatique. Les recommandations canadiennes pour la qualité des eaux douces (RCQE) relatives au glyphosate en vue de la protection de la vie en eau douce se rapportant à des expositions de courte et longue durée ont été élaborées selon le protocole du CCME (CCME, 2007) et selon la méthode statistique de type A, puisque le nombre de données disponibles était suffisant. Les distributions de la sensibilité des espèces (DES) ont été établies à l'aide du modèle log Fisher-Tippett pour les données d'exposition de courte et de longue durée. Les RCQE relatives aux expositions de courte et de longue durée au glyphosate sont respectivement de 27 000 et 800 µg m.a./L. Il est à noter que certaines formulations à base de glyphosate contiennent des surfactants qui sont plus toxiques que la matière active. Il est donc recommandé d'établir des recommandations spécifiques à ces surfactants ou d'appliquer des recommandations propres au site dans les régions où ces surfactants sont préoccupants.

Recommandation	**Valeur (µg m.a./L)**
Exposition de courte durée en eau douce	27 000*
Exposition de longue durée en eau douce	800**
Exposition de courte durée en eau marine	Aucune recommandation
Exposition de longue durée en eau marine	Aucune recommandation

* valeur calculée à partir des données de CL_{50} selon la méthode de la DSE

** valeur calculée à partir des concentrations à effet nul ou faible selon la méthode de la DES

Nota : Certaines formulations de glyphosate, y compris le Roundup, contiennent actuellement un surfactant qui peut être beaucoup plus toxique que le glyphosate lui-même. Il faut en tenir compte dans l'évaluation des données de surveillance et en cas de déversement direct de la substance dans des eaux de surface

1.0 INTRODUCTION

The Canadian Water Quality Guidelines (CWQG) for the Protection of Aquatic Life are developed through compilation and interpretation of aquatic toxicity data, thereby providing an important tool in the evaluation of ambient water quality. Glyphosate concentrations monitored in the environment can be compared to the guideline value to help predict whether sensitive species will be impacted in the ecosystem. Exceedance of the guideline values does not denote definite negative impacts to the environment, but rather an increased likelihood that effects may be observed and that further investigation is necessary, for example site-specific analysis of water chemistry parameters and sensitive species residing in the ecosystem.

The Water Quality Task Group of the Canadian Council of the Ministers of the Environment (CCME) is charged with overseeing the development of Canadian Water Quality Guidelines for the Protection of Aquatic Life. In 2007, the guideline derivation protocol was revised. The goals of the revised protocol include: (i) accounting for the unique properties of contaminants which influence their toxicity; and (ii) incorporating the species sensitivity distribution (SSD) method, which uses acceptable data as outlined in the protocol (provided these data pass quality control criteria) in a more flexible approach.

The structure of the criteria document for glyphosate has been built to accommodate the changes in the protocol for guideline derivation. All of the customary components of scientific criteria documents have been included (physical and chemical properties, production and uses, environmental fate and behaviour, environmental concentrations, toxicity data). In addition, new cornerstones of the protocol, such as bioaccumulation/bioconcentration, and toxicity modifying factors have been given attention.

2.0 PHYSICAL AND CHEMICAL PROPERTIES

Glyphosate is a non-selective, post-emergence organophosphorus (phosphonate class) herbicide used to control annual, perennial grasses and broad leaved weeds (British Crop Protection Council, 2000). The phosphonates, including glyphosate, differ from the other organophosphorus pesticides by having a P-C bond rather than the ester, P-O-C. The phosphonate P is reduced compared to the phosphates. The IUPAC chemical name of glyphosate is N-(phosphonomethyl)glycine and the CAS Registry Number is 1071-83-6. The chemical formula is $C_3H_8NO_5P$ and its chemical structure is illustrated in Figure 2.1.

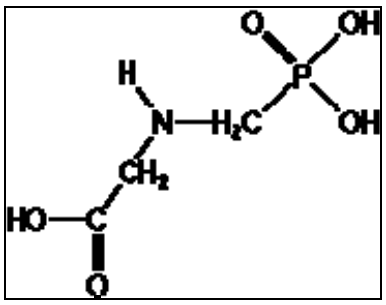

Figure 2- 1: Chemical Structure of Glyphosate

The physical and chemical properties of glyphosate are summarized in Table 2.1. Technical glyphosate, which is ≥95% pure, is presented as colorless crystals with a melting point of 189.5 ± 0.5°C and a specific density of 1.705 at 20°C. It is estimated Henry's Law constant of less than 2.1 x 10^{-7} Pa·m^3/mol and its vapour pressure of 1.31 x 10^{-5} Pa at 25°C suggest that it will be non-volatile and hence little evaporative loss will occur from water surfaces and it will not volatize from dry soils. Glyphosate is highly soluble in water (11.6 g/L at 25°C) and is insoluble in organic solvents. Glyphosate also tends to remain in water rather than to partition to organic substances having a log K_{ow} value of -3.22 and hence being hydrophilic. 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 (Hollis et al, 2004).

Glyphosate is used in several forms (not to be confused with formulations) to enhance absorption into the plant (Bradley, 2004). The glyphosate parent compound molecule is a weak organic acid that can be used in various salt forms such as the isopropylamine, the potassium, the trimethylsulfonium, and the diammonium salts. Toxicity data for all glyphosate forms were pooled in order to obtain the standard values as there is currently not enough evidence to demonstrate that the toxicity among the different salts differs and because the term glyphosate has generally been used to indicate all forms (Franz, 1985). In addition, the different salt forms roughly contain the same acid equivalent (± 10%) and there was no significant toxicity difference among the different salts in our dataset. The different glyphosate salt forms seem to influence the solubility, but not the overall biological activity (Franz, 1985).

Table 2-1: Physical and Chemical Properties of Glyphosate

Physical-Chemical Property	Glyphosate	Reference(s)
Appearance	White odorless crystals	(British Crop Protection Council, 2000)
Chemical Name (IUPAC)	N-(phosphonomethyl)glycine	(British Crop Protection Council, 2000)
Chemical Formula	$C_3H_8NO_5P$	(British Crop Protection Council, 2000)
CAS Number	1071-83-6	(British Crop Protection Council, 2000)
Specific density	1.705 at 20°C	(British Crop Protection Council, 2000)
Molecular Weight	169.1	(British Crop Protection Council, 2000)
Water Solubility	11.6 g/L at 25°C	(British Crop Protection Council, 2000)
Melting Point	189.5 ± 0.5°C	(British Crop Protection Council, 2000)
Vapour Pressure	1.31 x 10^{-5} Pa at 25°C	(British Crop Protection Council, 2000)
Partition Coefficient (log K_{ow})	< -3.2 at pH 2-5 at 20°C	British Crop Protection Council, 2000)
Partition Coefficient (log K_{oc})	28,000 mL/g	Hollis et al, 2004
Henry's constant	< 2.1 x 10^{-7} Pa m^3 mol^{-1}	(British Crop Protection Council, 2000)

2.1 Analytical Methods

Glyphosate residual analysis is a challenging task due to the physicochemical properties of the molecule. 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).

The first and the most widely used procedure to detect glyphosate in crops, animal tissues, soil, and water was developed by the manufacturer and referred to as the Monsanto procedure (Bardalaye et al., 1985). The method consists of an extraction, a subsequent clean-up on anion and cation exchange columns. Residue samples were then first derivatized by acetylation with trifluoroacetic acid and trifluoroacetic anhydride followed by a second derivatization by alkylation with diazomethane or O-methyl-N,N-dicyclohexyl pseudourea ether and detected by gas chromatography (GC) (Bardalaye et al., 1985; Stalikas and Konidari, 2001). Nevertheless, since this method suffered from irreproducible results, low recoveries, and use of highly toxic reagents, changes were made to improve the procedure (Stalikas and Konidari, 2001).

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). The initial derivatization reagents used in the Monsanto procedure resulted in high detection limits and poor reproducibility which prompted researchers to use different derivatives. The mixture of trifluoroethanol and trifluoroacetic anhydride (TFE-TFAA) was successful and resulted in better recoveries (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/L in water; 6 to 50 µg/kg in soil; 50 µg/kg for crops and 10 to 100 µg/kg in various animal products (Alferness and Iwata, 1994; Borjesson and Torstensson, 2000; Royer et al., 2000).

HPLC is a preferred approach in the analysis of glyphosate from water samples since derivatization is possible in aqueous solutions pre- and/or post-column (Stalikas and Konidari, 2001). The U.S. Environmental Protection Agency (EPA) glyphosate detection method from drinking water consists of an initial sample filtration, followed by separation through a cation-exchange column. Post-column derivatization is done with o-phthalaldehyde-2-mercaptoethanol which produces fluorophore that gets detected with a fluorometer (US EPA, 1990; Stalikas and Konidari, 2001). Soil samples can also be analyzed through HPLC using 1-fluoro-2,4-dinitrobenzene for derivatization. Despite being a good time efficient analytical technique, HPLC remains quite pricy (Stalikas and Konidari, 2001). HPLC methods have been successful in

different matrices (Stalikas and Konidari, 2001) with detection limits ranging from 6 to 50 µg/L in water (US EPA, 1990; Rubio et al., 2003).

The IC approach allows for a quick detection of hydrophilic substances and can also be used for glyphosate analysis. IC can be use with post-column derivation, ultra-violet (UV) detection and recently glyphosate can also be analyzed through suppressed conductivity IC (Zhu et al., 1999; Stalikas and Konidari, 2001). The reported detection limit for glyphosate in water using IC with suppressed conductivity detection or mass spectrometry ranges between < 1 to 42 µg/L (Bauer et al., 1999; Zhu et al., 1999; Guo et al., 2005).

Recent techniques to detect glyphosate include enzyme-linked immunosorbent assay (ELISA) and capillary electrophoresis (CE). The ELISA approach provides a cost effective and efficient method to detect glyphosate from environmental samples; nevertheless its initial high detection limit (76 to 100 µg/L with a pre-concentration step) was a significant barrier for its use (Clegg et al., 1999; Stalikas and Konidari, 2001). A derivatization of the sample before the ELISA allowed a significant improvement of the detection limit to 0.6 µg/L in water (Rubio et al., 2003). The EC approach has been reported for glyphosate detection in serum. The samples are initially derivatized with p-toluenesulphonyl chloride, then separated and detected in the UV region (Tomita et al., 1991). The authors did not report the detection limit of this method, but claimed a higher percent recovery than with other methods such as GC and HPLC. Other approaches using colorimetric, spectrophotometric, isotope, or thin layer chromatography (TLC) methods have been addressed, but were not retained to be used on a routine basis to detect glyphosate due to lack of specificity, high detection limits or other parameters.

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

3.0 PRODUCTION AND USES

In Canada, the Pest Management Regulatory Agency (PMRA) regulates the use of active ingredients under the *Pest Control Products* Act. Pesticides are registered for use in agricultural/forestry, industrial, and social applications. Provinces may impose additional restrictions on the use of the product. 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 (Table 3.1).

As a broad-spectrum, non-selective, systemic, and post-emergent herbicide, glyphosate targets essentially all annual and perennial plants (Franz et al., 1997). The broad-spectrum weed control property of the herbicide glyphosate has several applications. 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, 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).

Glyphosate has been registered for use in several countries and up to now has not been banned or restricted anywhere according to the US EPA Pesticide Action Network (PAN) pesticide database. Glyphosate is currently registered in Africa (Burkina Faso, Cameroon, Cape Verde, Chad, Gambia, Guinea-Bissau, Madagascar, Mali, Mauritania, Niger, Senegal, South Africa, Tanzania and Uganda), in Asia and in Pacific regions (Australia, New-Zealand and Philippines), in Europe (Denmark, European Union, Germany, Netherlands, Portugal, and the United Kingdom) and in North America (Canada and the United States).

It is difficult to obtain national pesticide sale data in Canada as only provincial systems are in place to collect pesticide sale data (Brimble et al., 2005). Brimble et al. (2005) reported on pesticide utilization in Canada, but acknowledged data inconsistencies between the provincial reports. Glyphosate is the most widely used herbicide in Canada with a total of 4,609,000 kg sold in 2002 (Brimble et al., 2005). Glyphosate is also the only herbicide to be used in all Canadian provinces that reported pesticide utilization data, Saskatchewan being the only province for which no data was acquired (Brimble et al., 2005). Alberta and Ontario have been identified as the dominant users of glyphosate using 3,419,822 kg (2003) and 1,170,762 kg (2003) of the herbicide active ingredient, respectively. Manitoba, British-Columbia, New-Brunswick, Nova Scotia, and Prince Edward Island also used significant amounts of glyphosate with 479,726 kg (2003), 126,269 kg (2003), 122,609 kg (2003), 17,218 kg (2003) and 8,999 kg (2002), respectively. Finally, Newfoundland and Labrador, the Yukon Territory and the Northwest Territories used substantially less glyphosate with only 428 kg (2003), 5 kg (1994) and 1 kg (1995), respectively (Brimble et al., 2005). No quantity of glyphosate sold in Quebec is available, nevertheless, glyphosate is known to be the most widely used herbicide in this province (Brimble et al., 2005). Preliminary data from 2008 suggests that glyphosate sales have increased dramatically (roughly 80%) since 2003 (personal communication, Gary Byrtus).

Recommended application doses and methods of glyphosate-based formulations vary between target species, species height and formulations themselves. Proposed applications methods include broadcast spray, hand-held equipment, high volume spray equipment, selection equipment (wiper and roller), injection systems and controlled droplet applicators. Aerial application is also an option for non-crop application. No matter the application method, all manufacturers are enforcing the importance of avoiding drifting and spraying on any body of water and on non-target areas/species. Timing of glyphosate application is also important and should be when the plants are close to maturity as pre-emergence application of glyphosate-based formulations would not affect vegetation survival. Additional information regarding the different application recommendation of the formulations can be found on the individual labels.

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 control of annual weeds range from 0.34 to 1.12 kg a.i. per ha and for perennials from 1.12 to 4.48 kg a.i. per ha applied in 187 to 561 L water per ha (Weed Science Society of America, 1989).

No data on the world production of glyphosate and its formulations are available. In addition, no data on losses to the environment during normal production, formulations, or accidental losses have been reported.

Table 3-1: List of the main glyphosate-based formulations used internationally. Currently there are 153 registered glyphosate products in Canada. Some formulations may contain surfactants which are more toxic than glyphosate.

Different forms of a single formulation are presented in a single row and specified in the second column. Adapted from the Weed Management PMRA, the PAN pesticide database, and the manufacturing companies

Formulation	Other forms	Mixture with other pesticide(s)	Company	Glyphosate salt	Glyphosate % a.i.	PMRA registered
Accord	Concentrate, XRT	NA	Dow AgroSciences	IPA	53.8	No
Afg	Original, Plus		Loveland products Inc.	IPA	41	No
Amega Max			NuFarm	IPA	NR	No
Andale			Monsanto	K+	NR	Yes
AquaMaster		NA	Monsanto	IPA	53.8	No
Bronco			Monsanto	K+	NR	Yes
Buccaneer	Plus		Tenkoz	IPA	41	No
Campaign		2.4-D	Monsanto	IPA	12.9	No
Catena		NA	Monsanto	IPA	41	No
ClearOut 41	Plus		Chemical Products Technologies LLC	IPA	41	Yes
Clinic	Pro, Duo, DT, EV, Aqua		NuFarm	IPA	NR	No
Cornerstone	Plus		Agriliance	IPA	41	No

Formulation	Other forms	Mixture with other pesticide(s)	Company	Glyphosate salt	Glyphosate % a.i.	PMRA registered
Credit *	Duo, Extra, Duo Extra		NuFarm	IPA or IPA+MA or IPA+DA	NR	Yes
Cutter			Monsanto	K+	NR	Yes
Drexel glyphosate	480, Plus, K max, 53.8%	NA	Drexel Chemical Co.	IPA	41 to 53.8	No
DupliKator 5.5 Plus		NA	Drexel	K+	48.8	No
Durango		NA	Dow AgroSciences	IPA	56.6	No
Eh	1386, 1387, 1389, 139	NA	Pbi/Gordon Corp	IPA	18 to 50	No
Extreme		Imazethapyr	BASF Ag	IPA	22	No
Fallow Master Broadspectrum		Dicamba	Monsanto	IPA	23.3	No
Field Master		Acetochlor, atrazine	Monsanto	IPA	8.2	No
Fireball		NA	Helena	Acid	11.4	No
Forza		NA	Cheminova Canada	IPA	30-60	No
Gf	772, 887, 1279	NA	Dow AgroSciences	IPA	41 to 53.6	No
Gly Star	Original, Plus, 5		Albaugh	IPA	41	No
Gly-4	Plus	NA	UCPA	IPA	41	No
Gly-Flo			Mycro Flo	IPA	41.5	No
Glyfos	X-TRA, Aquatic, PRO, Custom. Xtramax	NA	Cheminova	IPA	41.5	Yes
Glymix		2,4-D	Dow AgroSciences	IPA	41	No
Glyphogan		NA	Makhteshim Agan	IPA	41	No
Glyphomax	XRT	NA	Dow AgroSciences	IPA	NR	No
Glyphosate 4		NA	Vegetation Manager	IPA	41	No

Formulation	Other forms	Mixture with other pesticide(s)	Company	Glyphosate salt	Glyphosate % a.i.	PMRA registered
Glyphosate 4		NA	Farm$aver	IPA	41	No
Glyphosate 41 Plus		NA	Crop$mart	IPA	41	No
Glyphosate 41%		NA	Helm Agro US	IPA	41	No
Glyphosate Original		NA	Griffin	IPA	41	No
Glyphosate Pro	4, II	NA	Prokoz	IPA	41	No
Glyphosate T&O		NA	Quali-Pro	IPA	41	No
Glypro	Plus	NA	Dow AgroSciences	IPA	53.8	No
Helosate Plus			Helm Agro US	IPA	41	No
Herbamine		MCPA, diurion	NuFarm	NR	NR	No
Holster			Monsanto	K+	NR	Yes
Honcho	Plus	NA	Monsanto	IPA	41	No
Illico	TR, 2	Aminotriazole	NuFarm	NR	NR	No
Imitator Plus		NA	Drezel	IPA	41	No
Jardiflow		MCPA, diurion	NuFarm	NR	NR	No
Kernel		NA	Cheminova	Acid or IPA		
KleenUp			Verdicon - UAP	IPA	41	No
Lancer 400			NuFarm	NR	NR	No
Landmaster	BW, II	2.4-D	Monsanto	IPA	12.9	No
Makaze			UAP	IPA	41	No
Manage			Monsanto	K+	NR	Yes
Mirage *			UAP	IPA	NR	No

Formulation	Other forms	Mixture with other pesticide(s)	Company	Glyphosate salt	Glyphosate % a.i.	PMRA registered
Mon	14420, 8750, 14445, 77399, 78015, 78460, 78271, 78634	NA	Monsanto	K+ or IPA	41.0-48.7	Yes
Outlaw *			Monsanto	K+	NR	Yes
Pavanett EV		Dichlorprop, MCPA	NuFarm	NR	NR	No
Polado L		NA	Monsanto	IPA	53.8	No
QuickPRO		Diquat dibromide	Monsanto	Ammonium	73.3	No
Ranger PRO		NA	Monsanto	IPA	41	No
Rascal		NA	Agriliance	IPA	41	No
Rattler	Plus	NA	Helena	IPA	41	No
Rd	1617, 1626, 1629		Monsanto	K+	48.8	No
Renagade*			Monsanto	K+	NR	Yes
Rodeo®		NA	Monsanto and Dow AgroSciences	IPA	53.5 – 53.8	No
RoundUp	Original I, Original II, Original Max, Ultra, UltraDry, UltraMax, UltraMax II, WeatherMax, PRO, PRO Concentrate, PRODry		Monsanto	IPA	41	Yes
RT	3, Master II, 540	NA	Monsanto	K+	48.8	Yes
Rustler		Dicamba	Monsanto	IPA	23.3	Yes
ShootOut			Monsanto	K+	NR	Yes
Supersate*	UAP		UAP	IPA	NA	No

Formulation	Other forms	Mixture with other pesticide(s)	Company	Glyphosate salt	Glyphosate % a.i.	PMRA registered
Touchdown	Ct, HiTech, IQ, Total, 480, 600		Syngenta	K+ or DA	28.3-36.5	Yes
Vantage			Dow AgroSciences	IPA	NR	Yes
Vision		NA	Monsanto	IPA	41	Yes
Vision Max		NA	Monsanto	K+	49	Yes
Weemax GT		Aminotriazole	NuFarm	NR	NR	No
Wise Up			Mey corporation	IPA	41	No

NA: Not Applicable; NR: Not Reported; K+: Potassium salt, IPA: Isopropylamine salt, MA: Monoammonium salt, DA: Diammonium salt.

Formulations that were referenced in the literature but for which no information could currently be acquired through the distributors/registrants.

4.0 SOURCES TO THE ENVIRONMENT

Glyphosate may be introduced into the aquatic environment through spillage, accidental discharge, or waste disposal during production, storage, and use. When applied according to the label instructions glyphosate rarely reaches water sources directly (Bronstad and Friestad, 1985). The low vapour pressure of glyphosate suggests that loss by evaporation is not likely to occur (Bronstad and Friestad, 1985). Glyphosate is lost from static water rapidly, and from flowing water depending on flow rate (Franz et al., 1997). Manufacturer labels strongly advise users not to apply any glyphosate-based formulation directly 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 (Bronstad and Friestad, 1985). A higher concentration of glyphosate will enter the environment if rain occurs soon after application (Bronstad and Friestad, 1985).

Entry into the soil will occur at application, and glyphosate strongly binds to soil. Degradation can occur quite rapidly (Bronstad and Friestad, 1985). Wind erosion of soils from treated fields, particularly under dry conditions, can result in the distribution of glyphosate in the environment (Humphries et al., 2005). Glyphosate taken up by plants will eventually be found in soil as the plants decay (Bronstad and Friestad, 1985). Leachability of glyphosate is very low since it strongly binds to soil, and it is not sensitive to movement in runoff (Bronstad and Friestad, 1985).

5.0 ENVIRONMENTAL FATE AND BEHAVIOUR

5.1 Transformation Products

Transformation of glyphosate creates the metabolites aminomethylphosphonic acid (AMPA), N-methylaminomethylphosphonic acid, glycine, N,N-dimethylaminomethylphosphonic acid, and hydroxymethylphosphonic acid (Rueppel et al., 1977) (Figure 5.1). In both aerobic and anaerobic conditions, 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.

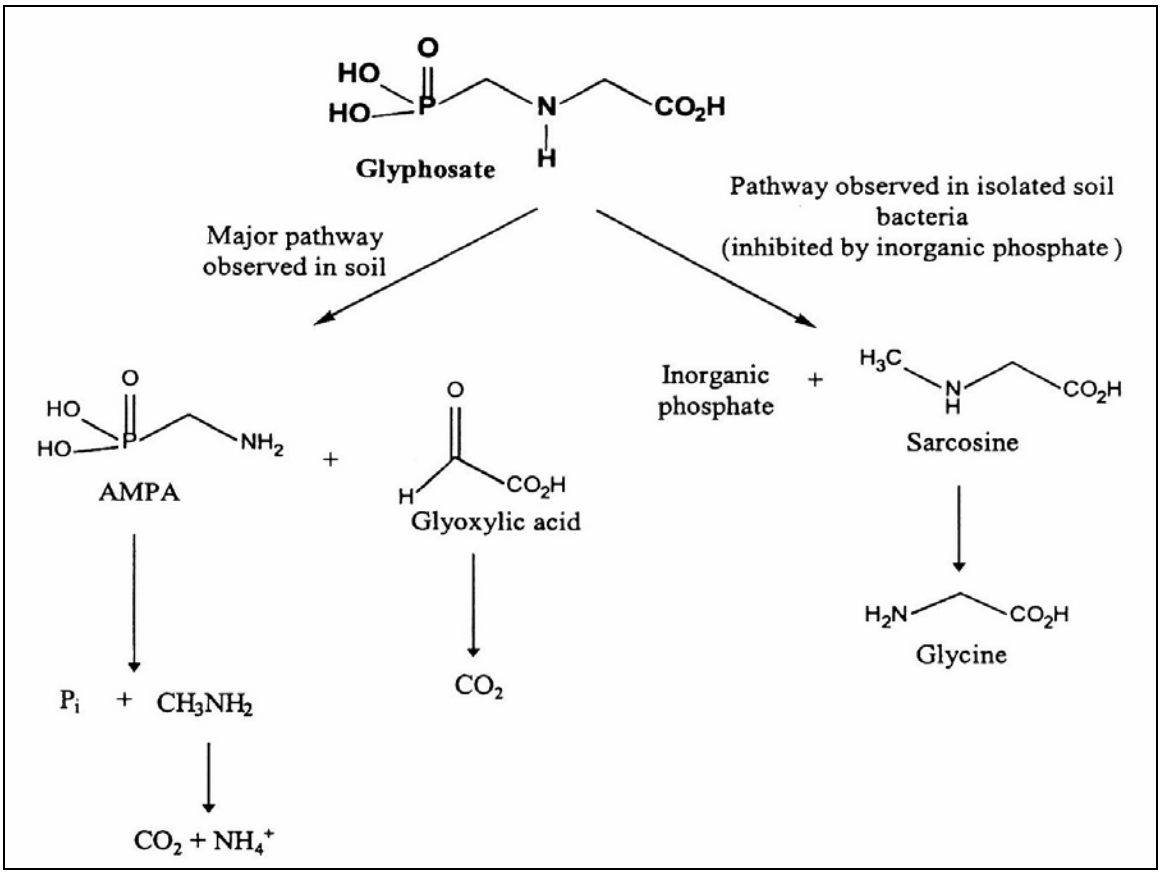

Figure 5-1: Structures of Glyphosate Transformation Products (from Giesy et al. 2000)

5.2 Fate in Water and Sediment

Glyphosate is highly soluble in water (11.6 g/L i.e., 11 600 000 µg/L) 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; Bronstad and Friestad, 1985). Zaranyika and Nyandoro (1993) support this, indicating that glyphosate in both water, and

sediment initially fades, and then decreases with time. In the formulation Round-Up, glyphosate has been shown to dissipate from water mainly due to binding to sediments (Bronstad and Friestad, 1985). The two main elements that explain the different behaviours of glyphosate in natural waters and distilled water are the presence of sediments, as glyphosate is strongly adsorbed by soil colloids, bottom silt, and suspended soil particles (Franz et al., 1997), and microflora in aquatic ecosystems.

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). In deionized water, sunlight has been reported to stimulate degradation (Franz et al., 1997). 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 (Hollis et al, 2004). Dissipation was reported to occur faster in the presence of high amounts of sediments in water (Wang et al., 1994b). 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, and reported photolytic half-lives at 100,000 µg/L and 2,000,000 µg/L were 4 days and 3 to 4 weeks, respectively (Lund-Hoie and Friestad 1986).

Microbial degradation of glyphosate, which will be covered in the soil section, also occurs in water (Bronstad and Friestad, 1985), but sediments and suspended particles were reported to be the major sink for glyphosate in water (WHO, 1994; Franz et al., 1997). Other potential herbicidal dissipation pathways do not seem to play a significant role in the degradation of glyphosate. When chemical degradation was studied in sterile soil, it was concluded that it was of little importance in the elimination of glyphosate (Rueppel et al., 1977; Bronstad and Friestad, 1985) and no evidence of the effect of physicochemical parameters such as pH or temperature have been reported. In sterile solutions, the chemical degradation of glyphosate is negligible (Sprankle et al., 1975c; Rueppel et al., 1977; Tooby, 1985; Bronstad and Friestad, 1985; Torstensson, 1985; all as cited in Franz et al., 1997).

Evidence from field studies confirms the behavior of glyphosate in the aquatic environment, as glyphosate rapidly dissipated from surface water of small forest ponds (Goldsborough and Beck, 1989). The authors also concluded that both sediment adsorption to suspended particulate matter, bottom sediments and microbial biodegradation were the major degradation pathways from the water. 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. However, other studies indicate that water contamination by direct spray is minimal (Franz et al., 1997).

5.3 Fate in Soil

Volatilization of glyphosate either from soil or water is not likely to occur (European Commission, 2002) as reflected by the very low value of the Henry's law constant ($< 2.1 \times 10^{-7}$ Pa m^3 /mol), and this was shown to be the case by Torstensson (1985).

Glyphosate is rapidly (within the first few hours (Torstensson, 1985)) adsorbed and tightly bound to most soils, indicating that it does not have significant pre-emergence herbicidal activity (Franz et al., 1997). Glyphosate adsorption happens within the first hour after treatment (Franz et al., 1997). Soil pH does not affect the adsorption of glyphosate (Sprankle et al., 1975b; Sprankle et al., 1975c; both as cited in Franz et al., 1997). Glyphosate has an initial rapid degradation followed by slower breakdown, due to early rapid metabolism of free glyphosate followed by slower degradation of soil-bound glyphosate (Carlisle and Trevors, 1988). In field studies, glyphosate disappeared rapidly in water, overstory foliage, litter, and penetration of glyphosate below the surface soil was negligible (Newton et al., 1984).

Glyphosate has little to no mobility in soil (nor does AMPA) (Rueppel et al., 1977; Newton et al., 1984; Franz et al., 1997) binding to the soil through its phosphonic acid moiety (Torstensson, 1985). However the mobility is slightly increased in soils with high pH and high levels of phosphate (Franz et al., 1997), as glyphosate competes with inorganic phosphates for binding sites. Glyphosate likely does not bind to the organic matter in soil, but rather other constituents (e.g., metal ions) in the charcoal and muck soil are responsible for binding (Franz et al., 1997). Various cations can affect the adsorption of glyphosate, depending on which cations are involved and what type of soil is being examined (Franz et al., 1997), though preferences have been noted for sodium and magnesium. It has been suggested that the increased adsorption of glyphosate by cation-saturated clay minerals indicates that glyphosate is complexed by cations released from the clay in a cation-exchange reaction with solution protons (Franz et al., 1997). Glyphosate is thought to be adsorbed within the interlayer spaces of the clay minerals (Franz et al., 1997). In soils with high sand content, glyphosate does not always bind as tightly, and may have some effect (Franz et al., 1997).

Degradation by microflora is the main route of degradation in soils (Sprankle et al., 1975c; Rueppel et al., 1977; Tooby, 1985; Bronstad and Friestad, 1985; Torstensson, 1985; Bujacz et al., 1995; all as cited in Franz et al., 1997), degrading glyphosate completely to carbon dioxide in soils and water (Rueppel et al., 1977; Bronstad and Friestad, 1985; Carlisle and Trevors, 1988). It is a co-metabolic process in aerobic and anaerobic soils (Sprankle et al., 1975b; Rueppel et al., 1977; Alexander, 1980;Torstensson et al., 1989; all as cited in Franz et al., 1997). However, microbial degradation depends on the free, colloidal particle adsorbed glyphosate and the microflora present (Bronstad and Friestad, 1985; Zaranyika and Nyandoro, 1993). Zaranyika and Nyandoro (1993) presented a enzymatic kinetic model proposing that glyphosate degradation is related to rate constants that are different for the glyphosate bound to sediment and for free glyphosate.

Chemical degradation is not a significant pathway of glyphosate degradation (Rueppel et al., 1977; Bronstad and Friestad, 1985). In sterile soils, the chemical degradation of glyphosate is negligible (Sprankle et al., 1975c; Rueppel et al., 1977; Tooby, 1985; Bronstad and Friestad, 1985; Torstensson, 1985; all as cited in Franz et al., 1997). However, in the presence of microflora, glyphosate rapidly, and completely biodegrades (Rueppel et al., 1977). Glyphosate dissipation rate is independent of concentration, but varies between the different types of soils. Glyphosate half-life in silt soil (86%) was three days while it was 27 days in a clay and silt soil. AMPA also completely degrades in soil; the average half-life in field studies using different soil types was reported to be two months (Sharp, 1974 as cited in Rueppel et al., 1997). Half-lives in soil are from less than a week up to years, depending on the level of microbial degradation and the extent of binding to the soil.

Other potential herbicidal dissipation pathways do not seem to play a significant role in the degradation of glyphosate. Due to strong binding to the soil and degradation, phytotoxic properties of glyphosate are negligible (Carlisle and Trevors, 1988). Sunlight has been reported to stimulate the degradation of glyphosate in soils. When chemical degradation was studied in sterile soil, it was concluded that it was of little importance in the elimination of glyphosate (Bronstad and Friestad, 1985). Leaching and runoff are also not significant pathways to dissipate glyphosate due to the high soil binding property of glyphosate (Rueppel et al., 1977; Bronstad and Friestad, 1985; Franz et al., 1997). This was supported by field studies in which no leaching occurred (Newton et al., 1984). Glyphosate is classified with the agricultural pesticides that are the least removed by runoff (Edwards et al., 1980). The concentration of glyphosate in runoff water is related to the time lapse between the herbicidal application and the rainfall with reported concentrations of glyphosate in runoff decreasing with time after treatment (Edwards et al., 1980). Even when glyphosate is detectable in runoff, a maximum of less than 2% of applied glyphosate could only be detected in runoff (Edwards et al., 1980). However, some studies (Sprankle et al., 1975b ;Rueppel et al., 1977; both as cited in Franz et al., 1997) indicate that these are very minor routes of breakdown of glyphosate in soils.

5.4 Fate in Vegetation

Initially, glyphosate is rapidly taken up by plant foliage (Franz et al., 1997), then the rate of uptake decreases over a longer period of time (Sprankle et al., 1975a; Richard and Slife 1979; Schultz and Burnside 1980; Caseley and Coupland, 1985; Masiunas and Weller 1988; Gaskin and Holloway 1992; Franz et al., 1997; all as cited in Franz et al., 1997). Several factors affect the mode and extent of glyphosate uptake in plants including the method of application, environmental characteristics, plant characteristics (e.g., species), glyphosate concentration, and other constituents in the formulation used (Caseley and Coupland, 1985).

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., 1975a; Gougler and Geiger, 1981; Foley et al., 1983).

The metabolism of glyphosate in plants has often been described as minimal to non-existent (Sprankle et al., 1975a ;Schultz and Burnside 1980; Caseley and Coupland, 1985).

5.5 Bioconcentration and Bioaccumulation

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 partition coefficient (Tooby, 1985; Wang et al., 1994b). Folmar et al. (1979) confirmed this, finding no residues of glyphosate or AMPA in fillets or eggs of rainbow trout exposed for 12h, nor were residues found in the early fourth instar larvae of *Chironomus plumosus*. Bengtsson et al. (2004) showed however, that after pre-exposure through diet, *Daphnia pulex* excreted glyphosate and that the body burden was reduced from 13 mg/g to 3 mg/g after 4 days. The authors also found a similar decrease if the pre-exposure was through water, from 50 mg/g to 10 mg/g.

The bioconcentration factor of Roundup, a glyphosate formulation, was reported to be 1.6 in bluegill sunfish (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).

6.0 CONCENTRATIONS IN CANADIAN WATERS

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 range; typical maximum observed concentrations were in the 10–20 µg a.i./L range. The maximum glyphosate concentration observed was 41 µg a.i./L. 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. 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 range. Among these samples, maximum concentrations were typically in the 20–30 µg a.i./L range. The sample with the maximum AMPA concentration observed was 66 µg/L (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 in 33% of the samples, with a maximum concentration of 12.0 µg a.i./L 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 and 13.832 µg a.i./L 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 dimethenamid (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.

7.0 GUIDELINES FROM OTHER JURISDICTIONS

The Canadian Council of Ministers of the Environment (CCME) has a published water quality guideline for the protection of aquatic life for glyphosate of 65 µg/L (CCME, 2006), and this value has been adopted by many provinces, including Saskatchewan, Alberta, and British Columbia. In contrast to the new guideline (which is developed using only toxicity data derived

using the active ingredient), this guideline was based on a formulated product containing glyphosate. Formulated products which include glyphosate (such as Roundup) may be more or less toxic than the active ingredient.

While drinking water guidelines are more prevalent worldwide, in most cases glyphosate in water is considered to not be harmful to human (WHO, 2005) or animal health (European Commission, 2002), and so guidelines for aquatic life are not determined. Drinking water guidelines vary worldwide, including lower values such as 10 μg/L in Australia (NHMRC, 2004) to higher values of 700 μg/L as the maximum contaminant level in the United States, and some in between, such as 280 μg/L in Canada (FPT Committee on Drinking Water, 2007).

8.0 AQUATIC TOXICITY

This section presents a review of the scientific literature on the toxicity of glyphosate to freshwater aquatic biota. All of the toxicity studies reviewed in this section are on the active ingredient of the pesticide, unless stated otherwise. The focus of the review is on the short-term (acute) and long-term (chronic) effects of glyphosate to survival, growth, and reproduction of aquatic organisms. Much of the aquatic toxicity data collected was from one of three sources, the U.S. EPA ECOTOX Database (2005), the European Commission (2002), and PMRA Summary (1997). Most studies were lacking a significant amount of information typically required for evaluation of the study, such as the physical-chemical parameters of the test conditions or the life stage of the test organism. However, the U.S. EPA ECOTOX Database, the European Commission, and PMRA Summary programs conduct thorough reviews of toxicity data for each substance as part of their registration requirements. Data received from these groups is generally submitted as confidential business information (CBI) and as such, the data available to the public are limited. Toxicity data received from these sources were assumed to have met the minimum data requirements outlined in the CCME (2007) Protocol. Effects data identified in the open literature were evaluated using the CCME (2007) data screening criteria for water quality guideline derivation. These criteria are designed to ensure that only high quality data are used. They distinguish studies as primary, secondary, or unacceptable according to whether or not sufficient information is provided to evaluate the study design, analyses, results, and other key parameters. Appendix A provides details on all of the aquatic toxicity studies reviewed, including their classification (primary, secondary, unacceptable) according to the CCME (2007) protocol. Studies failing to meet the requirements for primary or secondary classification are included in the following review, but were not considered in the CWQG derivation for freshwater aquatic biota exposed to glyphosate.

8.1 Mode of Action

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 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, as well as leaf wrinkling, or malformations (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.

8.2 Aquatic Toxicity

8.2.1 Freshwater

8.2.1.1 Fish

Results of short-term toxicity tests on a wide variety of species indicates glyphosate is relatively non-toxic (Atkinson 1985) (includes mammals).

Short-term Toxicity

There is a wealth of data available on the short-term toxicity of glyphosate to fish. The species of interest for which toxicity data was reported include bluegill sunfish (*Lepomis macrochirus*), channel catfish (*Ictalurus punctatus*), Chinook salmon (*Oncorhynchus tshawytscha*), chum salmon (*Oncorhynchus keta*), Coho salmon (*Oncorhynchus kisutch*), common carp (*Cyprinus carpio*), fathead minnow (*Pimephales promelas*), pink salmon (*Oncorhynchus gorbuscha*), and rainbow trout (*Oncorhynchus mykiss*).

Glyphosate has been determined to be relatively non-toxic to fish species. This is supported by the evidence in the literature. Bluegill sunfish, for example, have 24-h LC_{50}s ranging from 150,000 to 240,000 µg a.i./L, and 96-h LC_{50}s ranging from 2400 to >1,000,000 µg a.i./L (Folmar et al., 1979; Mayer and Ellersieck, 1986; US EPA,2007a,b,c). For channel catfish, 24-h LC_{50}s have been reported as 130,000 µg a.i./L (Folmar et al., 1979; Mayer and Ellersieck, 1986) and 96-h LC_{50}s range from 13,000 to 130,000 µg a.i./L (Folmar et al., 1979; Mayer and Ellersieck, 1986; US EPA,2007b,c).

Wan et al. (1989) looked at the effects of glyphosate in different water types on various species. They found that for Chinook salmon, 24-h LC_{50}s varied from 24,000-220,000 µg a.i./L, at 48-h the range was 22,000 to 220,000 µg a.i./L, at 72-h, it was 22,000 to 211,000 µg a.i./L, and at 96-

h it was 19,000 to 211,000 µg a.i./L. The results were similar when they looked at chum salmon, as 24-h LC_{50}s varied from 16,000 to 202,000 µg a.i./L, at 48-h the range was 13,000 to 178,000 µg a.i./L, at 72-h, it was 10,000 to 157,000 µg a.i./L, and at 96-h it was 10,000 to 148,000 µg a.i./L. For Coho salmon, the results indicated a slightly smaller range, with 24-h LC_{50}s from 44,000-210,000 µg a.i./L, 48-h LC_{50}s from 27,000-205,000 µg a.i./L, at 72-h the range was 27,000-182,000 µg a.i./L, and at 96-h it was 27,000-174,000 µg a.i./L. These results were consistent with those they found for pink salmon, as 24-h LC_{50}s varied from 26,000-380,000 µg a.i./L, at 48-h the range was 14,000-245,000 µg a.i./L, at 72-h, it was 14,000-190,000 µg a.i./L, and at 96-h it was 14,000-190,000 µg a.i./L.

The short-term toxicity of glyphosate to the common carp was examined by Ramaprabhu et al. (1991), who reported 24-h LC_{50}s of 6000 and 10,000 µg a.i./L. The fathead minnow is less sensitive, with reported 24-h LC_{50} values of 84,900 to 97,000 µg a.i./L (Folmar et al., 1979; Mayer and Ellersieck, 1986; US EPA, 2007b), and 96-h LC_{50}s of 9400 to 97,000 µg a.i./L (Folmar et al., 1979; Mayer and Ellersieck, 1986; US EPA, 2007b,c).

Rainbow trout 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 to 240,000 µg a.i./L (Folmar et al., 1979; Mayer and Ellersieck, 1986; Wan et al., 1989), at 48 and 72-h ranging from 11,000 to 220,000 µg a.i./L (Wan et al., 1989), and a range of 8200 to >1,000,000 µg a.i./L at 96-h (Folmar et al., 1979; Mayer and Ellersieck, 1986; Wan et al., 1989; US EPA,2007a,b,c). A 96-h LOEC for rainbow trout was reported as 8700 µg a.i./L (US EPA,2007b).

Long-term Toxicity

In contrast to the wealth of short-term toxicity data, little information is available on the long-term effects of glyphosate on freshwater fish. However the information available indicates that fish are not very sensitive to long-term glyphosate toxicity. Fathead minnows have a reported 255-d LOEC of 25,700 µg a.i./L (OPP Pesticides Database 2007), which was the most sensitive long-term endpoint found for fish. Early life stage Coho salmon had a reported 21-d NOEC of 130,000 µg a.i./L, which was similar to the 7-d NOEC of 150,000 µg a.i./L based on hatching success of rainbow trout (Graham van Aggelen (Environment Canada), pers. comm. 2007).

8.2.1.2 Invertebrates

Short-term Toxicity

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 3,000->1,000,000 µg a.i./L (US EPA,2007a; US EPA,2007b; US EPA, 2007c). The midge *Chironomus plumosus* had reported 48h LC/EC_{50}s of 13,000-55,000 µg a.i./L (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 a.i./L (US EPA, 2007b).

Very insensitive species of invertebrates included *Gammarus pseudolimnaeus*, with 48h LC_{50}s of 42,000 and 62,000 µg a.i./L (US EPA, 2007b) and *Mysidopsis bahia* (mysid shrimp) with a 96h LC_{50} of 40,000 µg a.i./L (US EPA, 2007a). Tsui and Chu (2003) reported a 40h IC_{50} (for growth) of 648,000 µg a.i./L for the ciliate *Tetrahymena pyriformis* and a 48h LC_{50} of 147,000 µg a.i./L for the amphipod *Ceriodaphnia dubia*.

Long-term Toxicity

Freshwater invertebrates were not very sensitive to glyphosate toxicity. *Ceriodaphnia dubia* had a reported 7d IC_{10} for reproduction of 65,600 µg a.i./L, and a 7d NOEC for mortality of >65,000 µg a.i./L (Summit Environmental Consultants Ltd, 2007). The USEPA Restricted database (2007c) reported 21d LOECs of 2,100 and 96,000 µg a.i./L and NOELs of 1,200 and 50,000 µg a.i./L for *Daphnia magna*. *Hyalella azteca* toxicity was reported by James Elphick (Summit Environmental Consultants Ltd., 2007), indicating a 14d EC_{10} of 53,900 µg a.i./L for survival and an IC_{10} for dry weight of 20 500 µg a.i./L, 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 and a NOEC/L of 1,000 µg a.i./L (Tate et al., 1997).

8.2.1.3 Algae and Aquatic Plants

Short-term Toxicity

Freshwater plants and algae are not very sensitive to short-term glyphosate toxicity. Studies of only three species were found. Cedergreen and Streibig (2005) tested the growth rate of *Pseudokirchneriella subcapitata* after 24h, reporting an EC_{50} of 270,000 µg a.i./L, and an EC_{10} of 92,500 µg a.i./L. The green algae *Chlorella fusca* had a reported 24h EC_{50} for population changes of 377,000 µg a.i./L (Faust et al., 1993), however these studies were run at temperatures that are considered quite high by Canadian standards (28 ± 0.5ºC). Duckweed (*Lemna minor*) was the most sensitive algae or aquatic plant species found, with reported 48h EC_{50}s of >16,910 µg a.i./L and 2,000 µg a.i./L (OPP Database, 2007).

Long-term Toxicity

Freshwater algae and aquatic plants are generally more sensitive to glyphosate toxicity than invertebrates and fish overall, however they are still relatively insensitive to glyphosate toxicity. The blue-green algae *Anabaena flos-aquae* had a reported 5d NOEL of 12,000 µg a.i./L (US EPA, 2007c), though the green algae *Chlorella pyrenoidosa* and *Chlorella vulgaris* had 96h EC_{50}s for growth inhibition of 3,530 and 4,696 µg a.i./L respectively (Ma et al., 2001; Ma et al., 2002). *Lemna gibba* was even more sensitive, with reported 14d NOELs of 1,400 and 1,800 µg a.i./L (US EPA, 2007c). Common water milfoil (*Myriophyllum sibiricum*) has a 14d IC_{50} for growth inhibition of 1,474 µg a.i./L (Roshon, 1997). The diatom *Navicula pelliculosa* had a reported 5d NOEL of 1,800 µg a.i./L, which was a fair bit more sensitive than the 5d NOEL for *Pseudokirchneriella subcapitata* of 10,000 µg a.i./L (US EPA, 2007c). Sago pondweed (*Potamogeton pectinatus*) had similar sensitivities as the snail described above, in that after 28 days of exposure, NOEC/L values for growth were 1,000 µg a.i./L, and LOEC/L values were 10,000 µg a.i./L (Fleming et al., 1991).

Three other species of green algae were reported in the literature, all of the same genus; *Scenedesmus acutus, S. obliquus, and S. quadricauda*. There was only one reported 96h EC_{50} for growth reported for *S. obliquus*, which was 55,858 µg a.i./L (Ma, 2002). Saenz et al. (1997) ran 96h tests on glyphosate toxicity, as shown by population changes, to *S. acutus*, resulting in EC_{50}s of 10,200 µg a.i./L, LOECs of 4,000 µg a.i./L, NOECs of 2,000 µg a.i./L, and MATC and ChV values of 2,820 µg a.i./L. They also examined the same endpoints in *S. quadricauda*, resulting in LOECs of 15 500 µg a.i./L, NOECs of 7 700 µg a.i./L, MATC and ChV values of 1,090 µg a.i./L, and EC50s of 7,200 µg a.i./L. Ma et al. (2003) also reported an EC_{50} for the same effect in that species, reporting a value of 70,500 µg a.i./L, almost an order of magnitude higher.

8.2.1.4 Amphibians

Short-term Toxicity

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 (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 (US EPA, 2007a). Green frogs (*Rana clamitans*) have reported 24 and 96-h LC_{50}s of > 38 900 µg a.i./L (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 µg a.i./L (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.

8.2.2 Marine

No marine studies on glyphosate toxicity were found.

8.3 Toxicity-Modifying Factors

Although water quality parameters such as hardness and pH have been examined as possible glyphosate toxicity modifying factors, there is currently not enough data to present conclusive evidence that there are any toxicity modifying factors for glyphosate. While there are some studies indicating that such factors may exist, when the data available from other studies is examined, no clear, conclusive relationship could be determined.

8.4 Toxicity of Transformation Products

Aminomethylphosphonic acid (AMPA) is the dominant and possibly the only conversion product of glyphosate (Bronstad 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 natural products used by organisms in the environment, it is unlikely that it is toxic at the levels indicating a threat to the environment (Bronstad and Friestad, 1985).

9.0 GUIDELINE DERIVATION

A CWQG for Glyphosate addresses its use in Canada and potential impacts to freshwater and marine aquatic systems. A CWQG provides guidance to risk assessors and risk managers in Canada on the level of glyphosate in an aquatic system, below which protection of the most sensitive species, and lifestage indefinitely is expected to be maintained.

There are currently three options for developing a CWQG (CCME, 2007). These consist of:

1. Statistical Approach (Type A or SSD approach);
2. Lowest Endpoint Approach using only primary data (Type B1);
3. Lowest Endpoint Approach using primary and/or secondary data (Type B2)

The minimum data requirements for each of the three methods are presented in Table 7.1, 7.2 (freshwater) and Table 7.3, 7.4 (marine). A SSD is a statistical distribution that represents the variation in toxicological sensitivity among a given set of species to a contaminant. The species sensitivity distribution, often expressed as a cumulative distribution function (CDF), is composed of effect concentrations obtained during toxicity testing (e.g., LC_{50}, EC_{50}, LOEL, or NOEL) on the horizontal axis and cumulative probability on the vertical axis (Posthuma et al. 2002). The number of data points used to construct the curve depends on the number of species tested for the endpoint of interest. Emphasis is placed on organism-level effects (e.g., survival, growth, reproduction) that can be more confidently used to predict ecologically significant consequences at the population level (Forbes and Calow 1999; Meador 2000; Suter II et al. 2005). With the SSD method, the concentration of a substance in water that will be protective of at least 95% of aquatic biota is estimated. For the purposes of a Canadian Water Quality Guideline we develop a short-term SSD based on acceptable short-term LC_{50} data. The guiding principle of a long-term SSD is to protect all of the species at all times, and is therefore based preferentially on long-term no-effect data.

If insufficient data are available for deriving a CWQG using the statistical approach, the CWQG will be developed using the next tier method, the lowest endpoint approach. Depending on the quantity and quality of data a Type B1 or Type B2 approach is used. The Type B1 approach uses acceptable primary toxicity data only to derive the guideline, while the Type B2 approach can use acceptable primary and/or secondary data. A safety factor is used in the derivation of a guideline using both Type B1 and B2 approaches. In every case, a CWQG must be developed using the most advanced method that the data allow.

The following sections describe the derivation of CWQGs for the protection of freshwater and marine life in surface water for the insecticide endosulfan. The derived CWQGs are national in scope and do not take into account watershed-specific conditions.

Table 9-1: Minimum Data Set Requirements for the Generation of short-term freshwater CWQG.

Group	Guideline		
	Type A	**Type B1**	**Type B2**
Fish	Three species, including at least one salmonid and one non-salmonid.		Two species, including at least one salmonid and one non-salmonid.
Aquatic Invertebrates	Three aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be either a mayfly, caddisfly, or stonefly.		Two aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be either a mayfly, caddisfly, or stonefly.
Plants	Toxicity data for aquatic plants or algae are highly desirable, but not necessary. However, if a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on non-target freshwater plant or algal species are required.		
Amphibians	Toxicity data for amphibians are highly desirable, but not necessary. Data must represent fully aquatic stages.		
Preferred Endpoints	Acceptable LC_{50} or equivalent (e.g., EC_{50} for immobility in small invertebrates).		
Data Quality Requirement	Primary and secondary LC_{50} (or equivalents) data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary LC_{50} (or equivalents) data. The value used to set the guideline must be primary.	The minimum data requirement must be met with primary LC_{50} (or equivalents) data. Secondary data are acceptable. The value used to set the guideline may be secondary.

Table 9-2: Minimum Data Set Requirements for the Generation of long-term freshwater CWQG.

Group	Guideline		
	Type A	**Type B1**	**Type B2**
Fish	Three species, including at least one salmonid and one non-salmonid.		Two species, including at least one salmonid and one non-salmonid.
Aquatic Invertebrates	Three aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be either a mayfly, caddisfly, or stonefly.		Two aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be either a mayfly, caddisfly, or stonefly.
Aquatic Plants	At least one study on a freshwater vascular plant or freshwater algal species. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and three studies on non-target freshwater plant or algal species are required.		Toxicity data for plants are highly desirable, but not necessary. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on non-target freshwater plant or algal species are required.
Amphibians	Toxicity data for amphibians are highly desirable, but not necessary. Data must represent fully aquatic stages.		Toxicity data for amphibians are highly desirable, but not necessary. Data must represent fully aquatic stages.
Preferred Endpoints	The acceptable endpoints representing the no-effects threshold and EC_{10}/IC_{10} for a species are plotted. The other, less preferred, endpoints may be added sequentially to the data set to fulfill the minimum data requirement condition and improve the result of the modelling for the guideline derivation if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: Most appropriate EC_x/IC_x representing a no-effects threshold > EC_{10}/IC_{10} > MATC > NOEC > $EC_{11\text{-}25}/IC_{11\text{-}25}$ > LOEC > $EC_{26\text{-}49}/IC_{26\text{-}49}$ > nonlethal EC_{50}/IC_{50}. Multiple comparable records for the same endpoint are to be combined by the geometric mean of these records to represent the averaged species effects endpoint.	The most preferred acceptable endpoint representing a low-effects threshold for a species is used as the critical study; the next less preferred endpoint will be used sequentially only if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: Most appropriate EC_x/IC_x representing a low-effects threshold > $EC_{15\text{-}25}/IC_{15\text{-}25}$ > LOEC > MATC > $EC_{26\text{-}49}/IC_{26\text{-}49}$ > nonlethal EC_{50}/IC_{50} > LC_{50}.	
Data Quality Requirement	Primary and secondary no-effects and low-effects level data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary data. The value used to set the guideline must be primary. Only low-effect data can be used to fulfill the minimum data requirement.	Secondary data are acceptable. The value used to set the guideline may be secondary. Only low-effect data can be used to fulfill the minimum data requirement.

Table 9-3: Minimum Data Set Requirements for the Generation of short-term marine CWQG.

Group	Guideline		
	Type A	**Type B1**	**Type B2**
Fish	At least three studies on three or more marine fish species, at least one of which is a temperate species.		At least two studies on two or more marine fish species, at least one of which is a temperate species.
Aquatic Invertebrates	At least two studies on two or more marine species from different classes, at least one of which is a temperate species.		At least two studies on two or more marine species.
Plants	At least **one** study on a temperate marine vascular plant or marine algal species. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on nontarget marine plant or algal species are required.		Toxicity data for marine plants are highly desirable, but not necessary. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on nontarget marine plant or algal species are required.
Preferred Endpoints	Acceptable LC_{50} or equivalent (e.g., EC_{50} for immobility in small invertebrates).		
Data Quality Requirement	Primary and secondary LC_{50} (or equivalents) data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary LC_{50} (or equivalents) data. The value used to set the guideline must be primary.	The minimum data requirement must be met with primary LC_{50} (or equivalents) data. Secondary data are acceptable. The value used to set the guideline may be secondary.

Table 9-4: Minimum Data Set Requirements for the Generation of long-term marine CWQG.

Group	Guideline		
	Type A	**Type B1**	**Type B2**
Fish	At least three studies on three or more marine fish species, at least one of which is a temperate species.		At least two studies on two or more marine fish species, at least one of which is a temperate species.
Aquatic Invertebrates	At least **two** studies on **two** or more marine species from different classes, at least **one** of which is a temperate species.		At least **two** studies on **two** or more marine species.
Plants	At least one study on a temperate marine vascular plant or marine algal species. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and three studies on nontarget marine plant or algal species are required.	At least one study on a temperate marine vascular plant or marine algal species. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on nontarget marine plant or algal species are required.	If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic and two studies on nontarget marine plant or algal species are required.
Preferred Endpoints	The acceptable endpoints representing the no-effects threshold and EC_{10}/IC_{10} for a species are plotted. The other, less preferred, endpoints may be added sequentially to the data set to fulfill the minimum data requirement condition and improve the result of the modelling for the guideline derivation if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: Most appropriate EC_x/IC_x representing a no-effects threshold > EC_{10}/IC_{10} > MATC > NOEC > $EC_{11\text{-}25}/IC_{11\text{-}25}$ > LOEC > $EC_{26\text{-}49}/IC_{26\text{-}49}$ > nonlethal EC_{50}/IC_{50}. Multiple comparable records for the same endpoint are to be combined by the geometric mean of these records to represent the averaged species effects endpoint.	The most preferred acceptable endpoint representing a low-effects threshold for a species is used as the critical study; the next less preferred endpoint will be used sequentially only if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: Most appropriate EC_x/IC_x representing a low-effects threshold > $EC_{15\text{-}25}/IC_{15\text{-}25}$ > LOEC > MATC $EC_{26\text{-}49}/IC_{26\text{-}49}$ > nonlethal EC_{50}/IC_{50} > LC_{50}.	
Data Quality Requirement	Primary and secondary no-effects and low-effects level data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary data. The value used to set the guideline must be primary. Only low-effect data can be used to fulfill the minimum data requirement.	Secondary data are acceptable. The value used to set the guideline may be secondary. Only low-effect data can be used to fulfill the minimum data requirement.

9.1 Protection of Freshwater Aquatic Life

The complete set of toxicity data considered for use in CWQG derivation (including data classified as primary, secondary) is presented in Appendix A. Unacceptable studies which were reviewed are not included in the table.

A CWQG provides guidance separately for both short and long-term exposure. The short-term guidance offered by the CWQG is not intended to protect all species indefinitely, but rather is to protect most species against lethality during severe, but transient events. Examples include inappropriate application or disposal of the pesticide in question. This may include application under worst case conditions and/or through improper use of label instructions (e.g. heavy precipitation/wind events), and spill events. The long-term exposure value of the CWQG is intended to protect against negative effects to all species and life stages during indefinite exposure. Aquatic life may be chronically exposed to a pesticide as a result of persistence in the environment, including gradual release from soils/sediments and gradual entry through groundwater/runoff, multiple applications within the same localized region, and long range transport events.

Short-term Benchmark Concentration

To be considered for inclusion in CWQG development, the aquatic toxicity studies must meet minimum data quality requirements as specified in the water quality protocol (CCME, 2007). Both primary and secondary data as described in the protocol (CCME, 2007) were considered acceptable for deriving the generic 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 were classified as primary data, unless erroneous values or other factors raised concerns about data quality. Much of the aquatic toxicity data collected for glyphosate was obtained from the following three sources: the U.S. EPA ECOTOX Database (2005), the European Commission (2001), and PMRA Summary (1997). Data received from these groups is generally submitted as confidential business information (CBI) and, as such, the data available to the public are limited.

Several of the studies reported in Appendix A are for the same species, effect, endpoint or life stage, though the LC_{50}s are different. This variation may be the result of differences in experimental conditions, species strain, and/or bioassay protocol. Multiple bioassay results for the same species should not be used in an SSD regression analysis. This is particularly important when there is a large amount of data available for very few test species. There are numerous methods that can be applied to account for multiple results for a single species (Duboudin et al., 2004). For the derivation of a CCME WQ guideline for glyphosate, intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive life stage and endpoint. The geometric means, in these cases, where taken for like species, life stage and endpoint. The final dataset was obtained from studies and endpoints deemed as acceptable (either of primary or secondary ranking) and from the endpoint deemed most acceptable for each species. The dataset for short-term SSD derivation from which the final SSD values were drawn is presented in Table 9.5.

Table 9-5 Final Aquatic Toxicity Data Selected For Generic SSD Development

Study No.	Organism	Latin Name	Effect	Effect Concentration (µg a.i./L)	Reference
1	Invertebrate	*Chironomus plumosus*	48-h LC_{50}	23434*	
2	Amphibian	*Litoria moorei*	96-h LC_{50}	29018*	
3	Fish	*Ictalurus punctatus*	96-h LC_{50}	30015*	
4	Amphibian	*Rana clamitans*	96-h LC_{50}	38900	Howe et al., 2004
5	Fish	*Oncorhynchus keta*	96-h LC_{50}	42372*	
6	Water Flea	*Daphnia pulex*	48-h LC_{50}	43724*	
7	Invertebrate	*Gammarus pseudolimnaeus*	48-h LC_{50}	51029*	
8	Amphibian	*Crinia insignifera*	96-h LC_{50}	55647*	
9	Fish	*Pimephales promelas*	96-h LC_{50}	56632*	
10	Fish	*Oncorhynchus gorbuscha*	96-h LC_{50}	56711*	
11	Fish	*Oncorhynchus tshawytscha*	96-h LC_{50}	66747*	
12	Fish	*Lepomis macrochirus*	96-h LC_{50}	67368*	
13	Fish	*Oncorhynchus mykiss*	96-h LC_{50}	68480*	
14	Fish	*Oncorhynchus kisutch*	96-h LC_{50}	73206*	
15	Water Flea	*Daphnia magna*	48-h LC_{50}	114709*	
16	Invertebrate	*Hyalella azteca*	96-h LC_{50}	144603*	
17	Water Flea	*Ceriodaphnia dubia*	48-h LC_{50}	147000	Tsui and Chu, 2003
18	Plant	*Pseudokirchneriella subcapitata*	24h EC50 (Growth rate)	270000	Cedergreen and Streibig, 2005
19	Plant	*Chlorella fusca*	24h EC50 (Population changes)	377000	Faust et al., 1993

***value shown is the geometric mean of comparable values, individual values and references can be seen in table 9.6**

Table 9-6 Studies Used To Derive Geometric Means for Short-term freshwater SSD

Organism	Endpoint	Effect Concentration (µg a.i./L)	Geometric Mean (µg a.i./L)	Reference
Ictalurus punctatus	96-h LC_{50}	130000	30015	Folmar et al., 1979
		13000		Office of Pesticide Programs, 2000
		16000		Office of Pesticide Programs, 2000
Lepomis macrochirus	96-h LC_{50}	2400	67368	Office of Pesticide Programs, 2000
		5800		Office of Pesticide Programs, 2000
		14000		Office of Pesticide Programs, 2000
		45000		Office of Pesticide Programs, 2000
		78000		Schuette, 1998
		120000		Weed Science Society of America, 1994
		134000		Office of Pesticide Programs, 2000
		135000		Johnson and Finley, 1980
		140000		Folmar et al., 1979
		220000		Mayer and Ellersieck, 1986
		230000		Office of Pesticide Programs, 2000
		830800		Office of Pesticide Programs, 2000
Oncorhynchus gorbuscha	96-h LC_{50}	14000	56711	Wan et al., 1989
		23000		Wan et al., 1989
		94000		Wan et al., 1989
		102000		Wan et al., 1989
		190000		Wan et al., 1989
Oncorhynchus keta	96-h LC_{50}	148000	42372	Wan et al., 1989
		22000		Wan et al., 1989
		99000		Wan et al., 1989
		10000		Wan et al., 1989
Oncorhynchus kisutch	96-h LC_{50}	27000	73206	Wan et al., 1989
		111000		Wan et al., 1989
		112000		Wan et al., 1989
		174000		Wan et al., 1989
		36000		Wan et al., 1989
Oncorhynchus mykiss	96-h LC_{50}	8200	68481	Office of Pesticide Programs, 2000
		8300		Office of Pesticide Programs, 2000
		10000		Wan et al., 1989
		22000		Wan et al., 1989
		38000		Schuette, 1998
		77600		Office of Pesticide Programs, 2000
		86000		Office of Pesticide Programs,

				2000
		86000		Trotter et al., 1990
		86000		Weed Science Society of America, 1994
		93000		Wan et al., 1989
		99000		Wan et al., 1989
		120000		Office of Pesticide Programs, 2000
		130000		Mayer and Ellersieck, 1986
		134000		Office of Pesticide Programs, 2000
		140000		Folmar et al.,1979
		140000		Mayer and Ellersieck, 1986
		150000		Office of Pesticide Programs, 2000
		197000		Wan et al. 2005
		240000		Office of Pesticide Programs, 2000
Oncorhynchus tshawytscha	96-h LC_{50}	102000	66748	Wan et al., 1989
		108000		Wan et al., 1989
		19000		Wan et al., 1989
		211000		Wan et al., 1989
		30000		Wan et al., 1989
Pimephales promelas	96-h LC_{50}	9400	56632	Office of Pesticide Programs, 2000
		67900		Office of Pesticide Programs, 2000
		97000		Mayer and Ellersieck, 1986
		97000		Trotter et al., 1990
		97000		Folmar et al., 1979
Chironomus plumosus	48-h LC_{50}	55000	23434	Folmar et al., 1979
		13000		Office of Pesticide Programs, 2000
		18000		Office of Pesticide Programs, 2000
Daphnia magna	48-h LC_{50}	3000	114709	Office of Pesticide Programs, 2000
		5300		Office of Pesticide Programs, 2000
		72000		Office of Pesticide Programs, 2000
		134000		Office of Pesticide Programs, 2000
		310000		Office of Pesticide Programs, 2000
		780000		Office of Pesticide Programs, 2000
		869000		Office of Pesticide Programs, 2000
		930000		Schuette, 1998
Daphnia pulex	48-h LC_{50}	242000	43724	Office of Pesticide Programs, 2000
		7900		Office of Pesticide Programs, 2000
Gammarus pseudolimnaeus	48-h LC_{50}	42000	51029	Office of Pesticide Programs, 2000
		62000		Office of Pesticide Programs, 2000

Hyalella azteca	96-h LC_{50}	160600 130200	144603	Summit Environmental Consultants Ltd., 2007 Summit Environmental Consultants Ltd., 2007
Crinia insignifera	96-h LC_{50}	78000 39700	55647	Office of Pesticide Programs, 2000 Office of Pesticide Programs, 2000
Litoria moorei	96-h LC_{50}	7600 110800	29018	US EPA Restricted Database, 2007 US EPA Restricted Database, 2007

Values used in the final SSD dataset range from a 96h-LC_{50} of 23434 µg/L for the invertebrate *Chironomus plumosus* to a 24h-EC_{50} for reproduction of 377,000 µg/L for the green algae *Chlorella fusca* (Office of Pesticide Programs, 2000; Faust et al., 1993). Geometric mean values were calculated for species where more than one EC/LC_{50} value was available for each for inclusion in the SSD. Effect concentrations reported for the remaining species were taken from single studies.

The short-term SSD was fitted using LC_{50} data and the final guideline value for glyphosate was the 5th percentile of the short-term SSD. Each species for which appropriate short-term toxicity data was available was ranked according to sensitivity, and its centralized position on the SSD was determined using the following standard equation (Aldenberg et al., 2002; Newman et al., 2002):

$$\frac{i - 0.5}{N}$$

where

i = the species rank based on ascending EC_{50}s and LC_{50}s
N = the total number of species included in the SSD derivation

These positional rankings, along with their corresponding EC_{50} and LC_{50}s were used to derive the SSD. Several cumulative distribution functions (CDFs) (normal, logistic, Gompertz, Weibull, Fisher-Tippett and Burr Type III) were fit to the data (both in arithmetic space and log space) using regression methods. Model fit was assessed using statistical and graphical techniques. The best model was selected based on consideration of goodness-of-fit and model feasibility. Model assumptions were verified graphically and with statistical tests.

The log Fisher-Tippett model provided the best fit of the twelve models tested (Anderson-Darling Statistic (A^2) = 0.247). The equation of the fitted logistic 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 fitted SSD derived using the log-Fisher-Tippett model and LC_{50} data for freshwater organisms is presented in Figure 9.1.

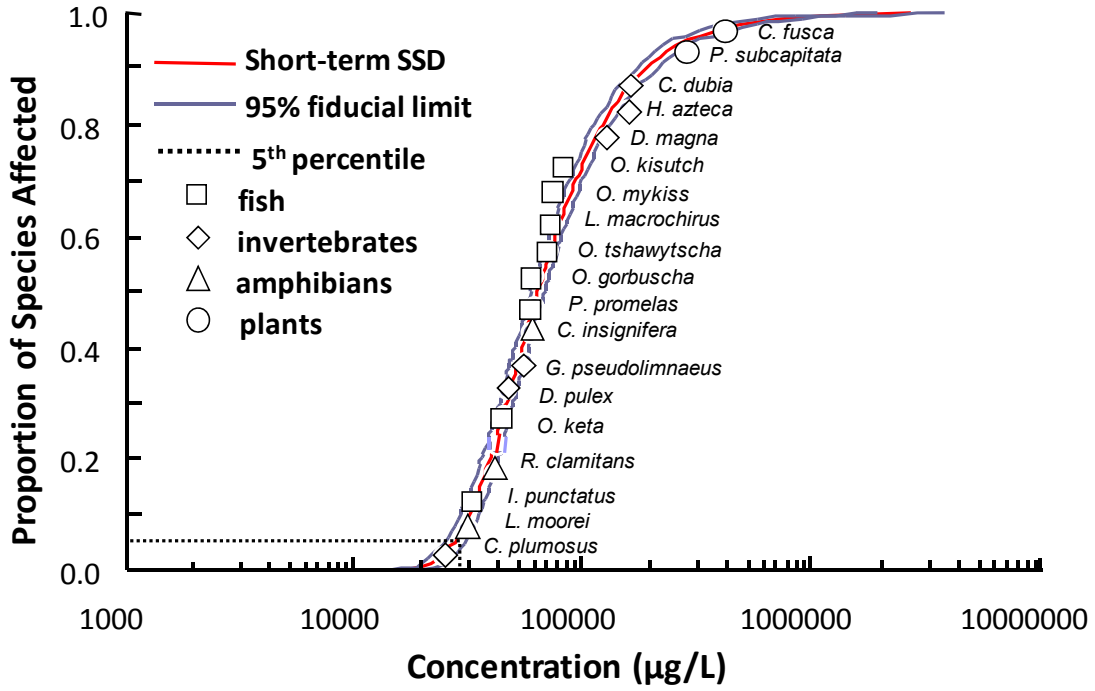

Figure 9- 1: Fitted Short-term SSD for Glyphosate.

The short-term SSD for freshwater aquatic organisms is presented in Figure 9.1. Summary statistics for the short-term SSD are presented in Table 9.4. The 5th percentile on the low effects short-term SSD is 27,000 µg a.i./L. The lower fiducial limit (5%) on the 5th percentile is 24,000 µg a.i./L, and the upper fiducial limit (95%) on the 5th percentile 30,500 µg a.i./L. The final short-term guideline value for glyphosate is the 5th percentile on the SSD.

Therefore, the Short-term CWQG value for protection of aquatic life in surface waters is 27,000 µg a.i./L for glyphosate.

Table 9- 7 Short-term CWQG for Glyphosate resulting from the SSD method.

Benchmark Concentration Metric	Concentration
SSD 5th percentile	**27,000 µg a.i./L**
SSD 5th percentile, 90% LFL (5%)	24,000 µg a.i./L
SSD 5th percentile, 90% UFL (95%)	30,500 µg a.i./L

Long-term CWQG

There were sufficient data to derive a long-term guideline using a generic SSD. Several of the studies reported in Appendix B are for the same species, effect, endpoint or life stage, though the values are different. This variation may be the result of differences in experimental conditions, species strain, and/or bioassay protocol. Multiple bioassay results for the same species should not be used in an SSD regression analysis. This is particularly important when there is a large amount of data available for very few test species. There are numerous methods that can be applied to account for multiple results for a single species (Duboudin et al., 2004). For the derivation of a guideline for glyphosate, intra-species variability was accounted for by taking the geometric mean of the studies considered to represent the most sensitive life stage and endpoint. The geometric means, in these cases, where taken for like species, life stage and endpoint. The final dataset was obtained from studies and endpoints deemed as acceptable (either of primary or secondary ranking) and from the endpoint deemed most acceptable for each species. For long-term guidelines, EC_{10}s are most preferred. Otherwise, the endpoint selection is, in order of preference: $EC_{10\text{-}30}$, MATC, NOEL, LOEL, and EC_{50}. The dataset for short-term SSD derivation from which the final SSD values were drawn is presented in Table 9.8.

Table 9-8 Final Aquatic Toxicity Data Selected For Generic SSD Development

Study No.	Organism	Latin Name	Effect	Effect Concentration (µg a.i./L)	Reference
1	Green Algae	*Scenedesmus quadricauda*	96-h MATC population changes	1,090*	Saenz et al., 1997
2	Plant	*Myriophyllum sibiricum*	14-d IC50 growth	1,474	Roshon, 1997
3	Plant	*Lemna gibba*	14-d NOEL	1,587*	US EPA Restricted Database, 2007
4	Diatom	*Navicula pelliculosa*	5-d NOEL	1,800	US EPA Restricted Database, 2007
5	Green Algae	*Scenedesmus acutus*	96-h MATC population changes	2,820*	Saenz et al., 1997
6	Plant	*Potamogeton pectinatus*	28-d MATC growth	3,162	Fleming et al., 1991
7	Invertebrate	*Pseudosuccinea columella*	12-d MATC Hatching success	3,162	Tate et al., 1997
8	Green Algae	*Chlorella pyrenoidosa*	96-h EC50 population growth inhibition	3,530	Ma et al., 2001

Table 9-8 Final Aquatic Toxicity Data Selected For Generic SSD Development

Study No.	Organism	Latin Name	Effect	Effect Concentration (µg a.i./L)	Reference
9	Green Algae	*Chlorella vulgaris*	96-h EC50 population growth inhibition	4,696	Ma et al., 2002
10	Green Algae	*Pseudokirchneriella subcapitata*	5-d NOEL	10,000	US EPA Restricted Database, 2007
11	Blue-green Algae	*Anabaena flos-aquae*	5-d NOEL	12,000	US EPA Restricted Database, 2007
12	Invertebrate	*Hyalella azteca*	14-d IC10 dry weight	20,500	Summit Environmental Consultants Ltd, 2007
13	Fish	*Pimephales promelas*	255-d LOEC	25,700	OPP PED, 2007
14	Water Flea	*Daphnia magna*	21-d geomean MATC	10487*	
15	Green Algae	*Scenedesmus obliquus*	96-h EC50 Population growth inhibition	55,858	Ma, 2002
16	Water Flea	*Ceriodaphnia dubia*	7-d NOEC mortality	65,000	Summit Environmental Consultants Ltd, 2007
17	Fish	*Oncorhynchus kisutch*	21-d early life stage NOEC	130,000	Graham van Aggelen (Environment Canada), pers. comm. 2007
18	Fish	*Oncorhynchus mykiss*	7-d NOEC hatching	150,000	Graham van Aggelen (Environment Canada), pers. comm. 2007

***value shown is the geometric mean of comparable values, individual values and references can be seen in table 9.9**

Table 9-9 Studies Used To Derive Geometric Means for Long-term freshwater SSD

Organism	Endpoint	Effect Concentration (µg a.i./L)	Geometric Mean (µg a.i./L)	Reference
Daphnia magna	21-d MATC	69282	10487	US EPA Restricted Database, 2007
		1587		US EPA Restricted Database, 2007
Scenedesmus quadricauda	96-h MATC	770	1090	Saenz et al., 1997
		1550		Saenz et al., 1997
Scenedesmus acutus	96-h MATC	2000	2820	Saenz et al., 1997
		4000		Saenz et al., 1997
Potamogeton pectinatus	28-d MATC	1000	3162	Fleming et al., 1991
		10000		Fleming et al., 1991
Pseudosuccinea columella	12-d MATC	1000	3162	Tate et al., 1997
		10000		Tate et al., 1997
Lemna gibba	14-d NOEC	1400	1587	US EPA Restricted Database, 2007
		1800		US EPA Restricted Database, 2007

Values used in the final SSD dataset range from a 96h-MATC for population changes of 1 090 µg a.i./L for the green algae *Scenedesmus quadricauda*, to a 7d-NOEC for hatching of 150 000 µg a.i./L for the fish (rainbow trout) *Oncorhynchus mykiss* (Saenz et al., 1997; Graham van Aggelen (Environment Canada), pers. comm. 2007). Geometric mean values were calculated for species where more than one value for the most preferred endpoint was available for each for inclusion in the SSD. Effect concentrations reported for the remaining species were taken from single studies.

The long-term SSD was fitted using acceptable data (MATCs, NOECs, IC_{50}s, etc.) and the final guideline value for glyphosate was the 5th percentile of the long-term SSD. Each species for which appropriate long-term toxicity data was available was ranked according to sensitivity, and its centralized position on the SSD was determined using the following standard equation (Aldenberg et al., 2002; Newman et al., 2002):

$$\frac{i - 0.5}{N}$$

where

i = the species rank based on ascending EC_{50}s and LC_{50}s
N = the total number of species included in the SSD derivation

These positional rankings, along with their corresponding long-term toxicity studies were used to derive the SSD. Several cumulative distribution functions (CDFs) (normal, logistic, Gompertz, Weibull, Fisher-Tippett and Burr Type III) were fit to the data (both in arithmetic space and log space) using regression methods. Model fit was assessed using statistical and graphical

techniques. The best model was selected based on consideration of goodness-of-fit and model feasibility. Model assumptions were verified graphically and with statistical tests.

The log Fisher-Tippett model provided the best fit of the twelve models tested (Anderson-Darling Statistic (A^2) = 0.284). The equation of the fitted Fisher-Tippett model is of the form:

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

where x is the concentration metameter, and the functional response, $f(x)$, is the proportion of taxa affected. The parameters, L and s, are the location and scale parameters of the model. The Gumbel distribution occurs when L is set to 0, and s is set to 1. The scale parameter in the Fisher-Tippett model must always be positive. For the fitted model L = 3.5994 and s = 0.6334.

The fitted SSD derived using the log-Fisher-Tippett model and long-term no and low-effect data for freshwater organisms is presented in Figure 9.2.

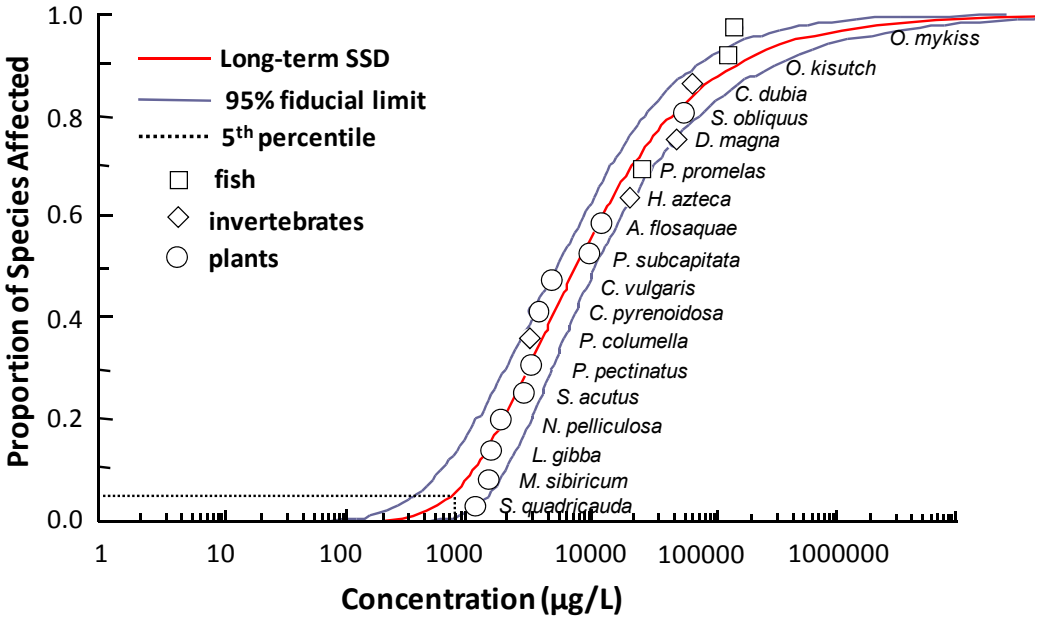

Figure 9-2: Fitted Long-term SSD for Glyphosate.

The long-term SSD for freshwater aquatic organisms is presented in Figure 9.2. Summary statistics for the long-term SSD are presented in Table 9.10. The 5th percentile on the low effects long-term SSD is 800 µg a.i./L. The lower fiducial limit (5%) on the 5th percentile is 490 µg a.i./L, and the upper fiducial limit (95%) on the 5th percentile is 1,320 µg a.i./L. The final long-term guideline value for glyphosate is the 5th percentile on the SSD.

Therefore, the Long-term CWQG value for glyphosate for protection of aquatic life in surface waters is 800 µg a.i./L for glyphosate.

Table 9-10 Long-term CWQG for Glyphosate resulting from the SSD method

CWQG Metric	Concentration
SSD 5th percentile	**800 µg a.i./L**
SSD 5th percentile, 90% LFL (5%)	490 µg a.i./L
SSD 5th percentile, 90% UFL (95%)	1,320 µg a.i./L

9.2 Protection of Marine Aquatic Life

At this time no acceptable marine toxicity tests were identified, thus no marine water quality guidelines were developed.

9.3 Data Gaps and Research Recommendations

There is a large body of available data concerning the short-term toxicity of technical glyphosate to freshwater fish and invertebrate species. Relatively speaking there is a paucity of long-term toxicology data. In the event that additional long-term freshwater toxicity test become available or are commissioned, it would be preferable that new long-term data generated would be available as EC_{10}s for incorporation in the long-term SSD. No acceptable marine studies for glyphosate were found. Additional studies would be useful in order to derive a short and long-term guideline value for the marine environment. It would be preferable that new long-term data generated would be available as EC_{10}s for incorporation in the long-term SSD.

9.4 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).

9.5 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.

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Appendix A:
Short-term Freshwater Toxicity Studies for Glyphosate

Acceptable short-term studies of the effects of glyphosate on aquatic organisms. Studies are deemed acceptable (either primary or secondary) or unacceptable using the criteria described in the Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life (CCME 1991).

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Amphibians									
Crinia insignifera (Sign-bearing froglet)	3d	96h LC50 (Mortality)	78000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Crinia insignifera (Sign-bearing froglet)	3d	96h LC50 (Mortality)	39700	NR	NR	NR		Office of Pesticide Programs, 2000	1
Litoria moorei (Western green tree frog)	Tadpole	96h LC50	7600	NR	NR	NR		US EPA Restricted Database, 2007	1
Litoria moorei (Western green tree frog)	Tadpole	96h LC50	110800	NR	NR	NR		US EPA Restricted Database, 2007	1
Rana clamitans (Green frog)	Gosner stage 25	24h LC50 (Mortality)	> 38900	7.8-8.3	20 ± 1	NR	Control mortality was not reported for the short-term studies and was not appropriate (38%) for the long-term study	Howe et al., 2004	2
Rana clamitans (Green frog)	Gosner stage 25	96h LC50 (Mortality)	> 38900	7.8-8.3	20 ± 1	NR	Control mortality was not reported for the short-term studies and was not appropriate (38%) for the long-term study	Howe et al., 2004	2
Fish									
Cyprinus carpio (Common carp)	NR	24h (Mortality)	10000	NR	NR	NR		Ramaprabhu et al., 1991	1
Cyprinus carpio (Common carp)	NR	24h (Mortality)	6000	NR	NR	NR		Ramaprabhu et al., 1991	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO 3/L)	Notes	Reference	Rank
Ictalurus punctatus (Channel catfish)	NR	24h LC50 (Mortality)	130000	7.2	22	40		Folmar et al., 1979	2
Ictalurus punctatus (Channel catfish)	0.5-2.2g	24h LC50 (Mortality)	130000	NR	NR	NR		Folmar et al., 1979	1
Ictalurus punctatus (Channel catfish)	NR	96h LC50 (Mortality)	130000	7.2	22	40		Folmar et al., 1979	2
Ictalurus punctatus (Channel catfish)	0.5-2.2g	96h LC50 (Mortality)	130000	NR	NR	NR		Folmar et al., 1979	1
Ictalurus punctatus (Channel catfish)	NR	96h LC50 (Mortality)	13000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Ictalurus punctatus (Channel catfish)	NR	96h LC50 (Mortality)	16000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lepomis macrochirus (Bluegill)	NR	24h LC50 (Mortality)	150000	7.2	22	40		Folmar et al., 1979	2
Lepomis macrochirus (Bluegill)	0.5-2.2g	24h LC50 (Mortality)	230000	NR	NR	NR		Folmar et al., 1979	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	2400	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	5800	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	14000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	45000	NR	NR	NR		Office of Pesticide Programs, 2000	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	78000	NR	NR	NR		Schuette, 1998	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	120000	NR	NR	NR		Weed Science Society of America, 1994	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	134000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lepomis macrochirus (Bluegill)	0.9g	96h LC50 (Mortality)	135000	NR	NR	NR		Johnson and Finley, 1980	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	140000	7.2	22	40		Folmar et al., 1979	2
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	220000	9.5	22	44		Mayer and Ellersieck, 1986	2
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	230000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	830800	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lepomis macrochirus (Bluegill)	NR	96h LC50 (Mortality)	>1000000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lepomis macrochirus (Bluegill)	0.54g	96h NOEL	32000	NR	NR	NR		US EPA Restricted Database, 2007	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	24h LC50 (Mortality)	26000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	24h LC50 (Mortality)	63000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	24h LC50 (Mortality)	94000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	24h LC50 (Mortality)	102000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	24h LC50 (Mortality)	380000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	48h LC50 (Mortality)	14000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	48h LC50 (Mortality)	34000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	48h LC50 (Mortality)	94000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	48h LC50 (Mortality)	102000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	48h LC50 (Mortality)	245000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	72h LC50 (Mortality)	14000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	72h LC50 (Mortality)	23000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	72h LC50 (Mortality)	94000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	72h LC50 (Mortality)	102000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	72h LC50 (Mortality)	190000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	96h LC50 (Mortality)	14000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	96h LC50 (Mortality)	23000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	96h LC50 (Mortality)	94000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	96h LC50 (Mortality)	102000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus gorbuscha (Pink salmon)	Juvenile	96h LC50 (Mortality)	190000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	24h LC50 (Mortality)	112000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	24h LC50 (Mortality)	202000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	24h LC50 (Mortality)	26000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	24h LC50 (Mortality)	16000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	48h LC50 (Mortality)	101000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	48h LC50 (Mortality)	178000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	48h LC50 (Mortality)	25000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	48h LC50 (Mortality)	13000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	72h LC50 (Mortality)	101000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	72h LC50 (Mortality)	157000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	72h LC50 (Mortality)	24000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	72h LC50 (Mortality)	10000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	96h LC50 (Mortality)	148000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus keta (Chum salmon)	Juvenile	96h LC50 (Mortality)	22000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	96h LC50 (Mortality)	99000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus keta (Chum salmon)	Juvenile	96h LC50 (Mortality)	10000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	24h LC50 (Mortality)	44000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	24h LC50 (Mortality)	132000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	24h LC50 (Mortality)	153000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	24h LC50 (Mortality)	210000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	24h LC50 (Mortality)	55000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	48h LC50 (Mortality)	27000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	48h LC50 (Mortality)	121000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	48h LC50 (Mortality)	122000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	48h LC50 (Mortality)	205000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	48h LC50 (Mortality)	37000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	72h LC50 (Mortality)	27000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	72h LC50 (Mortality)	115000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus kisutch (Coho salmon)	Juvenile	72h LC50 (Mortality)	117000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	72h LC50 (Mortality)	182000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	72h LC50 (Mortality)	36000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	96h LC50 (Mortality)	27000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	96h LC50 (Mortality)	111000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	96h LC50 (Mortality)	112000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	96h LC50 (Mortality)	174000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus kisutch (Coho salmon)	Juvenile	96h LC50 (Mortality)	36000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	24h LC50 (Mortality)	21000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	24h LC50 (Mortality)	32000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	24h LC50 (Mortality)	107000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	24h LC50 (Mortality)	115000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	NR	24h LC50 (Mortality)	130000	7	12	44		Mayer and Ellersieck, 1986	2
Oncorhynchus mykiss (Rainbow trout)	NR	24h LC50 (Mortality)	140000	7.2	12	40		Folmar et al., 1979	2
Oncorhynchus mykiss (Rainbow trout)	NR	24h LC50 (Mortality)	140000	NR	NR	NR		Trotter et al., 1990	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus mykiss (Rainbow trout)	Juvenile	24h LC50 (Mortality)	220000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	NR	24h LC50 (Mortality)	240000	6.5	12	44		Mayer and Ellersieck, 1986	2
Oncorhynchus mykiss (Rainbow trout)	NR	24h LC50 (Mortality)	240000	9.5	12	44		Mayer and Ellersieck, 1986	2
Oncorhynchus mykiss (Rainbow trout)	Juvenile	48h LC50 (Mortality)	11000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	48h LC50 (Mortality)	26000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	48h LC50 (Mortality)	107000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	48h LC50 (Mortality)	108000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	48h LC50 (Mortality)	220000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	72h LC50 (Mortality)	11000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	72h LC50 (Mortality)	22000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	72h LC50 (Mortality)	103000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	72h LC50 (Mortality)	108000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	72h LC50 (Mortality)	220000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	8200	NR	NR	NR		Office of Pesticide Programs, 2000	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	8300	NR	NR	NR		Office of Pesticide Programs, 2000	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus mykiss (Rainbow trout)	Juvenile	96h LC50 (Mortality)	10000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	96h LC50 (Mortality)	22000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	38000	NR	NR	NR		Schuette, 1998	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	77600	NR	NR	NR		Office of Pesticide Programs, 2000	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	86000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	86000	NR	NR	NR		Trotter et al., 1990	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	86000	NR	NR	NR		Weed Science Society of America 1994	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	96h LC50 (Mortality)	93000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	96h LC50 (Mortality)	99000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	120000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	130000	7	12	44		Mayer and Ellersieck, 1986	2
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	134000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	140000	7.2	12	40		Folmar et al., 1979	2

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	140000	6.5	12	44		Mayer and Ellersieck, 1986	2
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	150000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Oncorhynchus mykiss (Rainbow trout)	Juvenile	96h LC50 (Mortality)	197000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	240000	9.5	12	44		Mayer and Ellersieck, 1986	2
Oncorhynchus mykiss (Rainbow trout)	NR	96h LC50 (Mortality)	>1000000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Oncorhynchus mykiss (Rainbow trout)	26g	96h LOEC (Mortality)	8700	NR	NR	NR		Office of Pesticide Programs, 2000	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	24h LC50 (Mortality)	128000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	24h LC50 (Mortality)	157000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	24h LC50 (Mortality)	220000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	24h LC50 (Mortality)	24000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	24h LC50 (Mortality)	55000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	48h LC50 (Mortality)	108000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	48h LC50 (Mortality)	109000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	48h LC50 (Mortality)	22000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	48h LC50 (Mortality)	220000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	48h LC50 (Mortality)	30000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	72h LC50 (Mortality)	102000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	72h LC50 (Mortality)	108000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	72h LC50 (Mortality)	211000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	72h LC50 (Mortality)	22000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	72h LC50 (Mortality)	30000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	96h LC50 (Mortality)	102000	7.8 ± 0.04	14 ± 1	40 ± 0.5	Intermediate (reconstituted) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	96h LC50 (Mortality)	108000	7.8 ± 0.1	14 ± 1	68 ± 1.3	Intermediate (well) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	96h LC50 (Mortality)	19000	6.3 ± 0.03	14 ± 1	5.3 ± 0.2	Soft city water	Wan et al., 1989	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	96h LC50 (Mortality)	211000	8.2 ± 0.06	14 ± 1	86 ± 1	Hard (lake) water	Wan et al., 1989	1
Oncorhynchus tshawytscha (Chinook salmon)	Juvenile	96h LC50 (Mortality)	30000	7.2 ± 0.05	14 ± 1	10 ± 0.5	Soft creek water	Wan et al., 1989	1
Pimephales promelas (Fathead minnow)	NR	24h LC50 (Mortality)	84900	NR	NR	NR		Office of Pesticide Programs, 2000	1
Pimephales promelas (Fathead minnow)	NR	24h LC50 (Mortality)	97000	7.4	20	44		Mayer and Ellersieck, 1986	2
Pimephales promelas (Fathead minnow)	NR	24h LC50 (Mortality)	97000	NR	NR	NR		Trotter et al., 1990	1
Pimephales promelas (Fathead minnow)	NR	96h LC50 (Mortality)	9400	NR	NR	NR		Office of Pesticide Programs, 2000	1
Pimephales promelas (Fathead minnow)	NR	96h LC50 (Mortality)	67900	NR	NR	NR		Office of Pesticide Programs, 2000	1
Pimephales promelas (Fathead minnow)	NR	96h LC50 (Mortality)	97000	7.4	20	44		Mayer and Ellersieck, 1986	2
Pimephales promelas (Fathead minnow)	NR	96h LC50 (Mortality)	97000	NR	NR	NR		Trotter et al., 1990	1
Pimephales promelas (Fathead minnow)	NR	24h LC50 (Mortality)	97000	7.2	22	40		Folmar et al., 1979	2
Pimephales promelas (Fathead minnow)	NR	96h LC50 (Mortality)	97000	7.2	22	40		Folmar et al., 1979	2

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO3/L)	Notes	Reference	Rank
Invertebrates									
Ceriodaphnia dubia (Water flea)	NR	48h LC50 (Mortality)	147000	8.07	25 ± 1	69.5		Tsui and Chu, 2003	2
Ceriodaphnia dubia (Water flea)	NR	48h LC50 (Mortality)	>280000	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Ceriodaphnia dubia (Water flea)	NR	48h LC10 (Mortality)	127400	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Chironomus plumosus (Midge)	4th instar	48h EC50 (Immobility)	55000	7.2	22	40		Folmar et al., 1979	2
Chironomus plumosus (Midge)	NR	48h LC50 (Mortality)	13000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Chironomus plumosus (Midge)	NR	48h LC50 (Mortality)	18000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	3000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	5300	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	72000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	134000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	310000	NR	NR	NR		Office of Pesticide Programs, 2000	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO 3/L)	Notes	Reference	Rank
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	780000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	869000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	>1000000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h EC50 (Immobilization)	>22000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia magna (Water flea)	NR	48h LC50 (Mortality)	930000	NR	NR	NR		Schuette, 1998	1
Daphnia magna (Water flea)	<24 hr	48h NOEL	100000	NR	NR	NR		US EPA Restricted Database, 2007	1
Daphnia pulex (Water flea)	NR	48h EC50 (Immobility)	242000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Daphnia pulex (Water flea)	NR	48h EC50 (Immobility)	7900	NR	NR	NR		Office of Pesticide Programs, 2000	1
Gammarus pseudolimnaeus (Scud)	NR	48h LC50 (Mortality)	42000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Gammarus pseudolimnaeus (Scud)	NR	48h LC50 (Mortality)	62000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Hyalella azteca (Amphipod)	NR	96h EC50 (Survival)	160600	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Hyalella azteca (Amphipod)	NR	96h EC50 (Survival)	130200	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg CaCO 3/L)	Notes	Reference	Rank
Hyalella azteca (Amphipod)	NR	96h EC25 (Survival)	126400	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Hyalella azteca (Amphipod)	NR	96h EC10 (Survival)	122600	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Mysidopsis bahia (Mysid shrimp)	NR	96h LC50 (Mortality)	40000	NR	NR	NR		US EPA, 2007a	1
Tetrahymena pyriformis (Ciliate)	NR	40h IC50 (Growth)	648000	7.4	27 ± 1	NR		Tsui and Chu, 2003	2
Aquatic Plants and Algae									
Chlorella fusca (Green algae)	Synchronized culture	24h EC50 (Population changes)	377000	NR	28 ± 0.5	NR	Study details taken from Altenburger et al., 1990	Faust et al., 1993	2
Lemna minor (Duckweed)	NR	48h EC50 (Abundance)	>16910	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lemna minor (Duckweed)	NR	48h EC50 (Abundance)	2000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Pseudokirchneriella subcapitata (Green algae)	NR	24h EC10 (Growth rate)	92500	8	22	NR		Cedergreen and Streibig, 2005	2
Pseudokirchneriella subcapitata (Green algae)	NR	24h EC50 (Growth rate)	270000	8	22	NR		Cedergreen and Streibig, 2005	2

h=hour; d=day; ELS=Early life stage; LC=Life cycle; NR=Not reported; NOEC/L=No observable effect concentration/level; LOEC/L=Lowest observable effect concentration/level; MATC=Maximum Allowable Toxicant Concentration; EC=Effect Concentration; IC=Inhibition Concentration; LC=Lethal Concentration

Appendix B:
Long-term Freshwater Toxicity Studies for Glyphosate

Acceptable long-term studies of the effects of glyphosate on aquatic organisms. Studies are deemed acceptable (either primary or secondary) or unacceptable using the criteria described in the Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life (CCME 1991).

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg $CaCO_3$/L)	Notes	Reference	Rank
Fish									
Oncorhynchus kisutch (Coho salmon)	ELS	21d NOEC	130000	NR	NR	NR		Graham van Aggelen (Environment Canada), pers. comm. 2007	1
Oncorhynchus mykiss (Rainbow trout)	NR	7d NOEC (Hatching success)	150000	NR	NR	NR		Graham van Aggelen (Environment Canada), pers. comm. 2007	1
Pimephales promelas (Fathead minnow)	LC	255d LOEC	25700	NR	NR	NR		Office of Pesticide Programs, 2000	1
Invertebrates									
Ceriodaphnia dubia (Amphipod)	NR	7d EC50 (Mortality)	84600	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Ceriodaphnia dubia (Water flea)	NR	7d NOEC (Mortality)	>65000	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Ceriodaphnia dubia (Water flea)	NR	7d IC50 (Reproduction)	83900	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Ceriodaphnia dubia (Water flea)	NR	7d IC25 (Reproduction)	72000	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Ceriodaphnia dubia (Water flea)	NR	7d IC10 (Reproduction)	65600	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Daphnia magna (Water flea)	LC	21d LOEC	2100	NR	NR	NR		US EPA Restricted Database, 2007	1

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg $CaCO_3$/L)	Notes	Reference	Rank
Daphnia magna (Water flea)	LC	21d LOEC	96000	NR	NR	NR		US EPA Restricted Database, 2007	1
Daphnia magna (Water flea)	LC	21d NOEL	1200	NR	NR	NR		US EPA Restricted Database, 2007	1
Daphnia magna (Water flea)	LC	21d NOEL	50000	NR	NR	NR		US EPA Restricted Database, 2007	1
Hyalella azteca (Amphipod)	NR	14d EC50 (Survival)	144100	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Hyalella azteca (Amphipod)	NR	14d EC25 (Survival)	85900	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Hyalella azteca (Amphipod)	NR	14d EC10 (Survival)	53900	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Hyalella azteca (Amphipod)	NR	14d IC50 (Dry weight)	135500	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Hyalella azteca (Amphipod)	NR	14d IC25 (Dry weight)	29800	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Hyalella azteca (Amphipod)	NR	14d IC10 (Dry weight)	20500	NR	NR	NR		Summit Environmental Consultants Ltd., 2007	1
Pseudosuccinea columella (Snail)	NR	12d LOEC/L (Hatching success)	10000	6.5-8.5	NR	80-120		Tate et al., 1997	2

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg $CaCO_3$/L)	Notes	Reference	Rank
Pseudosuccinea columella (Snail)	NR	12d NOEC/L (Hatching success)	1000	6.5-8.5	NR	80-120		Tate et al., 1997	2
Aquatic Plants and Algae									
Anabaena flosaquae (Blue-green algae)	NR	5d EC50 (Abundance)	15000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Anabaena flosaquae (Blue-green algae)	NR	5d NOEL	12000	NR	NR	NR		US EPA Restricted Database, 2007	1
Anabaena flosaquae (Blue-green algae)	NR	96h EC50 (Abundance)	11750	NR	NR	NR		Office of Pesticide Programs, 2000	1
Chlorella pyrenoidosa (Green algae)	Population	96h EC50 (Population growth inhibition)	3530	NR	25	NR		Ma et al., 2001	2
Chlorella vulgaris (Green algae)	Population	96h EC50 (Population growth inhibition)	4696	NR	25	NR		Ma et al., 2002	2
Lemna gibba (Inflated duckweed)	NR	14d EC50 (Abundance)	12400	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lemna gibba (Inflated duckweed)	NR	14d EC50 (Abundance)	21500	NR	NR	NR		Office of Pesticide Programs, 2000	1
Lemna gibba (Inflated duckweed)	NR	14d NOEL	1400	NR	NR	NR		US EPA Restricted Database, 2007	1
Lemna gibba (Inflated duckweed)	NR	14d NOEL	1800	NR	NR	NR		US EPA Restricted Database, 2007	1
Lemna minor (Duckweed)	NR	7d EC10 (Growth rate)	3780	5	24	NR		Cedergreen and Streibig, 2005	2
Lemna minor (Duckweed)	NR	7d EC50 (Growth rate)	46900	5	24	NR		Cedergreen and Streibig, 2005	2

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg $CaCO_3$/L)	Notes	Reference	Rank
Myriophyllum sibiricum (Common water milfoil)	NR	14d IC50 (Growth)	1474	NR	NR	NR	Used medium for serial dilution	Roshon, 1997	2
Navicula pelliculosa (Diatom)	NR	5d EC50 (Abundance)	17000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Navicula pelliculosa (Diatom)	NR	5d NOEL	1800	NR	NR	NR		US EPA Restricted Database, 2007	1
Navicula pelliculosa (Diatom)	NR	7d EC50 (Abundance)	38600	NR	NR	NR		Office of Pesticide Programs, 2000	1
Navicula pelliculosa (Diatom)	NR	7d NOEL	19100	NR	NR	NR		US EPA Restricted Database, 2007	1
Potamogeton pectinatus (Sago pondweed)	NR	28d NOEC/L (Growth)	1000	NR	20-23	NR		Fleming et al., 1991	2
Potamogeton pectinatus (Sago pondweed)	NR	28d LOEC/L (Growth)	10000	NR	20-23	NR		Fleming et al., 1991	2
Pseudokirchneriella subcapitata (Green algae)	NR	5d EC50 (Abundance)	14000	NR	NR	NR		Office of Pesticide Programs, 2000	1
Pseudokirchneriella subcapitata (Green algae)	NR	5d EC50	14000	NR	NR	NR		US EPA Restricted Database, 2007	1
Pseudokirchneriella subcapitata (Green algae)	NR	5d NOEL	10000	NR	NR	NR		US EPA Restricted Database, 2007	1
Pseudokirchneriella subcapitata (Green algae)	NR	7d EC50 (Abundance)	12540	NR	NR	NR		Office of Pesticide Programs, 2000	1
Pseudokirchneriella subcapitata (Green algae)	Population	96h EC50 (Population growth inhibition)	7800	NR	24 ± 2	NR		St-Laurent et al., 1992	2

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg $CaCO_3$/L)	Notes	Reference	Rank
Pseudokirchneriella subcapitata (Green algae)	NR	96h EC50	12540	NR	NR	NR		US EPA Restricted Database, 2007	1
Pseudokirchneriella subcapitata (Green algae)	NR	96h EC50	12540	NR	NR	NR		US EPA, 2007a	1
Pseudokirchneriella subcapitata (Green algae)	NR	96h IC50 (Growth)	24700	7.5	25 ± 1	NR		Tsui and Chu, 2003	2
Scenedesmus acutus (Green algae)	Population	96h ChV (Population growth inhibition)	2820	7.5	22 ± 1	80.1		Saenz et al., 1997	2
Scenedesmus acutus (Green algae)	Population	96h EC50 (Population growth inhibition)	10200	7.5	22 ± 1	80.1		Saenz et al., 1997	2
Scenedesmus acutus (Green algae)	Population	96h EC50 (Population changes)	10200	NR	NR	NR		Saenz et al., 1997	2
Scenedesmus acutus (Green algae)	Population	96h LOEC (Population changes)	4000	NR	NR	NR		Saenz et al., 1997	2
Scenedesmus acutus (Green algae)	Population	96h LOEC/L (Population growth inhibition)	4000	7.5	22 ± 1	80.1		Saenz et al., 1997	2
Scenedesmus acutus (Green algae)	Population	96h MATC (Population changes)	2820	NR	NR	NR		Saenz et al., 1997	2
Scenedesmus acutus (Green algae)	Population	96h NOEC (Population changes)	2000	NR	NR	NR		Saenz et al., 1997	2
Scenedesmus acutus (Green algae)	Population	96h NOEC/L (Population growth inhibition)	2000	7.5	22 ± 1	80.1		Saenz et al., 1997	2
Scenedesmus obliquus (Green algae)	Population	96h EC50 (Population growth inhibition)	55858	NR	25	NR		Ma, 2002	2

Organism	Life stage	Endpoint	Effect concentration (µg a.i./L)	pH	Temp. (ºC)	Hardness (mg $CaCO_3$/L)	Notes	Reference	Rank
Scenedesmus quadricauda (Green algae)	Population	96h ChV (Population growth inhibition)	1090	7.5	22 ± 1	80.1		Saenz et al., 1997	2
Scenedesmus quadricauda (Green algae)	Population	96h EC50 (Population growth inhibition)	70500	NR	NR	NR		Ma et al., 2003	2
Scenedesmus quadricauda (Green algae)	Population	96h EC50 (Population growth inhibition)	7200	7.5	22 ± 1	80.1		Saenz et al., 1997	2
Scenedesmus quadricauda (Green algae)	Axenic	96h EC50 (Population changes)	7200	NR	NR	NR		Saenz et al., 1997	2
Scenedesmus quadricauda (Green algae)	Axenic	96h LOEC (Population changes)	1550	NR	NR	NR		Saenz et al., 1997	2
Scenedesmus quadricauda (Green algae)	Population	96h LOEC/L (Population growth inhibition)	1550	7.5	22 ± 1	80.1		Saenz et al., 1997	2
Scenedesmus quadricauda (Green algae)	Axenic	96h MATC (Population changes)	1090	NR	NR	NR		Saenz et al., 1997	2
Scenedesmus quadricauda (Green algae)	Axenic	96h NOEC (Population changes)	770	NR	NR	NR		Saenz et al., 1997	2
Scenedesmus quadricauda (Green algae)	Population	96h NOEC/L (Population growth inhibition)	770	7.5	22 ± 1	80.1		Saenz et al., 1997	2

h=hour; d=day; ELS=Early life stage; LC=Life cycle; NR=Not reported; NOEC/L=No observable effect concentration/level; LOEC/L=Lowest observable effect concentration/level; MATC=Maximum Allowable Toxicant Concentration; EC=Effect Concentration; IC=Inhibition Concentration; LC=Lethal Concentration