Aquatic herbicide applications for the control of aquatic plants in Canada: Effects to nontarget aquatic organisms

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REVIEW

Aquatic herbicide applications for the control of aquatic plants in Canada: effects to nontarget aquatic organisms

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Abstract: Nuisance growths of aquatic plants in Canadian surface waters continue to be problematic. Only diquat, a contact herbicide that is used to control many free-floating plants (but is less effective at controlling emergent plants), is registered in Canada for general aquatic use. Other herbicides are currently only permitted under "emergency registration." Recent emergency registrations have been granted to glyphosate and imazapyr, and these two herbicides are likely candidates to be proposed for full registration for direct application to water in Canada in the foreseeable future. These herbicides have been extensively studied in laboratory conditions and have provided a benchmark for ecotoxicity for a variety of aquatic organisms, yet the inherent toxicity of these herbicides derived from tests does not always translate into their environmental toxicity in natural aquatic ecosystems as the fate (e.g., removal from the water body via binding to sediments and suspended solids, degradation, volatization, etc.) and exposure (i.e., continuous in the laboratory versus "pulsed" in the field) of herbicides in the natural environment is very different from their fate and exposure in laboratories. These differences will likely result in field studies having lower biological effects than laboratory studies, even if the initial exposure concentrations were similar. This review details the current knowledge based on field studies that examine the effects of the direct application of diquat, glyphosate, and imazapyr to aquatic environments on aquatic organisms. The studies of the effects of the aquatic formulations of diquat, glyphosate, and imazapyr that are reviewed here generally found negligible or short-lived impacts on fish and aquatic invertebrates in situ, whereas they found that the application of these herbicides was often beneficial through the physical modification of available habitat (i.e., an increase in open water outweighs any potential toxic effects). Conversely, certain surfactants used to increase herbicide efficacy have been suggested to be more toxic than the herbicide itself. We thus suggest monitoring the effects associated with controlled applications of diquat and other aquatic herbicides including glyphosate and imazapyr and their surfactants, as this would be a means of accumulating information that may guide future uses of herbicides in Canadian waterways.

Key words: aquatic herbicide, fish, invertebrate, amphibian, glyphosate, diquat.

Résumé : La prolifération de plantes aquatiques dans les eaux de surface canadiennes continue d'être problématique. Seulement le diquat, un herbicide de contact utilisé pour contrôler un grand nombre de plantes flottantes libres (mais moins efficace au niveau du contrôle des plantes émergentes) est homologué au Canada aux fins d'utilisation aquatique générale. On permet actuellement les autres herbicides uniquement sous « licence d'utilisation d'urgence ». On a récemment accordé des licences d'utilisation d'urgence à glyphosate et à imazapyr et ces deux herbicides sont, dans un avenir prévisible, des candidats probables à être soumis pour homologation complète pour application directe dans l'eau au Canada. Ces herbicides ont été largement étudiés dans des conditions de laboratoire et ont fourni un point de référence pour l'écotoxicité touchant une variété d'organismes aquatiques, pourtant la toxicité intrinsèque de ces herbicides découlant de tests ne se traduit pas toujours par leur toxicité environnementale dans les écosystèmes aquatiques naturels parce que le devenir des herbicides dans l'environnement naturel (p. ex., leur élimination du plan d'eau en se liant aux sédiments et aux matières en suspension, par dégradation, par volatisation, etc.) et leur exposition (c.-à-d., continue dans le laboratoire par rapport à « pulsée » dans le milieu) diffèrent grandement de leur devenir et de leur exposition en laboratoire. Ces différences donneront probablement lieu à des recherches in situ montrant des effets biologiques moindres que les études de laboratoire, même si les concentrations d'exposition initiales sont semblables. Cette revue présente en détail la connaissance actuelle fondée sur les recherches in situ examinant les effets de l'application directe de diquat, de glyphosate et d'imazapyr dans les milieux aquatiques, et ce, sur les organismes aquatiques. Les recherches sur les effets des formulations aquatiques de diquat, de glyphosate et d'imazapyr qui sont passées en revue ici ont généralement révélé des impacts négligeables ou éphémères sur les poissons et les invertébrés aquatiques in situ, tandis qu'elles ont montré que l'application de ces herbicides était souvent avantageuse par la modification physique de l'habitat disponible (c.-à-d., l'augmentation de l'eau libre compense pour les effets toxiques possibles). Au contraire, certains agents de surface utilisés pour augmenter l'efficacité des herbicides pourraient être, selon les données, plus toxiques que l'herbicide lui-même. Nous suggérons ainsi de surveiller les effets liés aux applications contrôlées de diquat et d'autres herbicides aquatiques, y compris le glyphosate et l'imazapyr et leurs agents de surface, car ceci serait un moyen d'accumuler des informations qui peuvent orienter les utilisations d'herbicides dans les voies navigables canadiennes à l'avenir. [Traduit par la Rédaction]

Mots-clés : herbicide en milieu aquatique, poisson, invertébré, amphibien, glyphosate, diquat.

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Introduction

Nuisance growths of native and invasive aquatic plants continue to be problematic in Canadian surface waters. These nuisance weeds can impede conveyance and hamper recreational and commercial activities, such as beach going, swimming, boating, and fishing, while also potentially negatively impacting the physical, chemical, and biological characteristics of the waterbody. The control of aquatic plants is variously permitted in Canada depending on the provincial or federal jurisdiction, but controls are generally limited to physical removal methods, despite the fact that chemical controls are less expensive and more thorough than other means (Netherland 2014; Hussner et al. 2017). In Canada, only one herbicide, diquat (Reward Aquatic Herbicide, Syngenta Canada Inc., Guelph, Ontario), is currently registered for general aquatic use under a permit (copper complexes are registered for use as algaecides in ponds, lagoons, dugouts, and potable water tanks but not in lakes and rivers, and acrolein (Magnicide H) is registered for use only in irrigation canals; OMAFRA 2016). Reward Aquatic Herbicide, according to the product label, is used for the control of "weeds in still or slow-moving water of farm dugouts, farm ponds, industrial ponds, farm ditches, lakes, streams and canals." Diquat thus has a widespread use and is effective at controlling free-floating weeds, such as Duckweed (*Lemna* spp.) and Watermeal (*Wolffia*), yet it is comparatively ineffective at removing many emergent weeds, such as Common Reed (*Phragmites*) and Cattails (*Typha* spp.; Netherland 2014; OMAFRA 2016). Diquat is a contact herbicide; it is nonmobile in the plant, only affecting the part of the plant that it comes into contact with (Netherland 2014). These contact herbicides are known as "knockdown" herbicides as they provide effective seasonal control but not effective eradication of rooted plants as they do not directly affect the roots (Sinnott 2015), leading to regrowth of the plant, whereas systemic herbicides are mobile, translocating through the plant via the phloem or xylem (Netherland 2014). Movement through these transport systems enables the herbicide to affect all parts of the plant, above and below ground, ensuring that there is no recovery or regrowth. Systemic herbicides, such as glyphosate and imazapyr, are thus better suited to control emergent and submergent plants than contact herbicides (Netherland 2014) such as diquat.

In Canada, the use of herbicides other than diquat to directly control aquatic plants is occasionally permitted, but currently only under "emergency registration" from Health Canada's Pest Management Regulatory Agency (PMRA). An emergency registration was granted in 2016, for example, to treat 500 ha of marsh habitat with glyphosate and the adjuvant Aquasurf, a systemic herbicide, in Long Point, Lake Erie, to control *Phragmites* (OMNRF 2016). Imazapyr, also a systemic herbicide, has been used since 2013 with the surfactant Ag-Surf II to control, for example, Cordgrass (*Spartina* spp.) in tidal mudflats along the British Columbia (BC) coast (HTC 2016), and it was approved in 2016 to control the emergent Flowering Rush (*Butomus umbellatus*) in Lake Isle, Alberta (Government of Alberta 2017). The two active ingredients used in these examples, glyphosate (Roundup Custom Aquatic formulation) and imazapyr (Habitat Aqua), are expected to be the two most likely candidates to be proposed for full registration and may become the most commonly used actives, along with diquat, for direct application to Canadian waters in the foreseeable future. PMRA is Canada's agency that evaluates the risks of new and existing pesticides to the Canadian environment and Canadians. When evaluating a pesticide for registration, PMRA reviews all existing scientific studies that meet certain criteria related to toxicity to invertebrates and fish (amphibian bioassays are not currently required by PMRA (PMRA 2000; HC 2005) or the Canadian Council of Ministers of the Environment (CCME 2007). Evaluation decisions can be made with as little as one study for each criterion, provided the standard is met (PMRA 2000), and field studies examining the toxicological effects on nontarget aquatic organisms may not be a requirement for registration of a pesticide (HC 2005). The present nonfield-based models and scenarios cannot be used for direct aquatic application as they cannot reliably simulate the dilution, dispersion, or downstream movement or the fate processes that would happen in the natural aquatic environment.

Herbicides are a class of pesticides that are designed to be inherently toxic to their target organisms (plants). These herbicides can also be highly toxic to nontarget organisms, especially in aquatic environments. Indeed, laboratory (lab) studies have shown that trace amounts of these toxic chemicals have severe effects on nontarget biota. Exposure to diquat, for example, at concentrations of 0.04 mg/L for 3 days (chronic exposure) resulted in the death of 50% (i.e., the LC_{50}) of the amphipod, *Hyalella azteca* (Wilson 1968). Herbicides are typically applied to waterbodies at much higher doses than the LC_{50} found for some species in lab studies (e.g., Wilson 1968; Pless 2005; Netherland 2014), implying that they may cause serious negative impacts to the aquatic community. There is thus a hesitation to approve their uses in these environments, yet the inherent toxicity of herbicides as evidenced from lab studies may not always translate into environmental toxicity in the natural aquatic environment (e.g., Gardner and Grue 1996; Simenstad et al. 1996; Tremblay 2004), as the fate of herbicides in the natural environment might be very different from their fate in the lab. Indeed, in natural environments, herbicides are subjected to many physical, chemical, and biological processes that they are not necessarily subjected to in lab studies (reviewed in Mangels 1991; US EPA 1993, 1995, 2006; Gibs 1998; Siemering and Hayworth 2005). Lab studies of toxic effects may also be more pronounced than field studies due to the role of exposure. Lab studies use a method of continual exposure (i.e., concentrations are maintained at the initial exposure level for the duration of the experiment) whereas field studies experience "pulsed" exposure, whereby the herbicide is applied over a finite period of time (a single application, spray over for one day, etc.) and thus concentrations will decrease over time due to various environmental factors, such as adsorption, degradation, and volatilization, reducing the contact time between the herbicide and nontarget organisms, which would potentially result in lower toxicity to these nontarget organisms. These differences will likely result in field studies having lower biological effects than lab studies, even if the initial dosage is the same. However, field studies of direct applications of aquatic herbicides to aquatic systems are lacking in numbers and scope. For imazapyr, for example, there is only one microcosm study on aquatic invertebrates conducted in Florida with which to base informed management decisions pertaining to the use of this herbicide in Canadian aquatic systems.

The intent of this literature review is to summarize field studies on diquat, glyphosate, and imazapyr as these are the herbicides that are, or may shortly become, registered for use in Canadian aquatic systems. Specifically, the risks these herbicides pose to aquatic animals under the scenario of direct application to freshwater environments will be reviewed. This review considers both the spatial and temporal aspects of exposure and effects of these herbicides on aquatic organisms, specifically in natural field, limnocorral, and micro- and mesocosm environments. In terms of being applicable to Canadian environments, this review first considers direct applications to Holarctic freshwater systems, where possible.

Diquat

Diquat, used for aquatic applications in Canada since 2000, is the only herbicide currently registered for general aquatic use in Canadian waterways. In the United States and New Zealand diquat was first registered for aquatic use in the 1960s (Clayton 1986; Netherland 2014) and has also been registered in Australia and

Table 1. Summary of the acute and chronic L(E)C_{50} concentration (mg/L) ranges of aquatic invertebrates, fish, and amphibians exposed to aquatic formulations of diquat, glyphosate, and imazapyr in laboratory studies extracted from the US ECOTOX Database (24 November 2017).

		Diquat		Glyphosate		Imazapyr	
Taxa	Exposure	Min	Max	Min	Max	Min	Max
Aquatic Invertebrates	Acute	**0.120**	100	**0.100**	5600	>0.91 (6.60)	>1750
	Chronic	**0.048**	260	4.80	1177	132	189
Fish	Acute	**0.750**	5967	**0.530**	620	>0.91 (2.71)	>1000
	Chronic	**1.500**	9.8	—	—	—	—
Amphibians	Acute	140	340	—	—	—	—
	Chronic	—	—	—	—	—	—

Note: Bolded values represent LC_{50} concentrations that are under typical field application concentrations. Values in parenthesis represent lowest reported definitive LC_{50} concentrations.

other countries including Brazil and Mexico (Hussner et al. 2017 and references therein). This herbicide is a broad-spectrum contact herbicide that is used to control free-floating weeds, including Duckweed, *Salvinia*, Water Lettuce (*Pistia*), and Watermeal, and submersed plants in areas of high dilution (Netherland 2014; OMAFRA 2016; Hussner et al. 2017).

The ecological risk of diquat is minimized due to diquat having a very short exposure time (Siemering et al. 2008). Diquat thus has a low propensity for bioconcentration and bioaccumulation (Petit et al. 1995; BLM 2005 and references therein). Bioaccumulation in Bluegill Sunfish (*Lepomis macrochirus*), for example, exposed to approximately 1 mg/L diquat for 30 days in ponds contained approximately 0.09 mg/g diquat residue (Cope 1966).

Typical applications of diquat result in dose concentrations of about 0.1–0.4 mg/L in water (Netherland 2014). Published lab studies on the LC_{50} of both fresh and salt water fish and amphibians and the LC_{50} and EC_{50}[1] (L(E)C_{50}) of both fresh and salt water aquatic invertebrates exposed to aquatic formulations of the three herbicides reviewed here were extracted from the US Environmental Protection Agency's (EPA) ECOTOX Database (https://cfpub.epa.gov/ecotox/; accessed on 24 November 2017; Table 1). These endpoints (L(E)C_{50}) were used rather than more subtle nonlethal endpoints (e.g., behaviour, enzyme activity, developmental processes, etc.) because most field studies reviewed here examined parameters related to survival (e.g., mortality, abundance, presence, etc.) and thus direct comparisons can be made. The studies obtained from the ECOTOX search were then divided into acute (here defined as ≤7 d for fish and amphibians and ≤72 h for invertebrates) and chronic (here defined as >7 d for fish and amphibians and >72 h for invertebrates) exposures. The L(E)C_{50} values for both acute and chronic studies of fish and aquatic invertebrates exposed to aquatic formulations of diquat ranged from well below typical field concentrations, with aquatic invertebrates displaying lower tolerances, to orders of magnitude above. There was only one study of amphibians under these parameters, and it displayed LC_{50} values well above the natural field concentrations. These results suggest that when typical doses are applied diquat is largely non- or slightly toxic (based on inherent-toxicity classification schemes) to most species in a lab setting, except for certain invertebrates.

Despite diquat being the only herbicide registered for aquatic use in Canada, there have been relatively few field studies documenting effects on nontarget organisms, and none of the published studies has been conducted in Canada. There is an ongoing study funded by Fisheries and Oceans Canada (DFO), examining the effects of this herbicide in ecologically relevant lab (i.e., pulsed rather than continual exposure) and mesocosm settings (e.g., DFO 2017; Dalton et al. unpublished data[2]); considering diquat has been used in Canadian waters for almost 20 years, this study is long overdue. There are two field studies examining the effects on aquatic organisms of the direct application of aquatic formulations of diquat to waterways in somewhat similar climates to Canada: in northern United States and in England. First, Wilson (1968) studied the effects of 2.5 mg/L diquat on aquatic invertebrates in two Soap Creek Ponds in Oregon, USA. There were no differences between control and treatment plots in the number of benthic Tendipedidae (a subfamily of Chironomidae midges) or in littoral *Caenis*, *Callibaetis* (both mayflies), *Coenagrionidae* (damselflies), *Libellulidae* (dragonflies), Sialidae (alderflies), and Talitridae (amphipods). Given the results, Wilson (1968) concluded that diquat poses negligible risks to invertebrates when applied to natural aquatic systems. Mortality, development, and activity were studied in free-living populations of the Smooth Newt (*Triturus vulgais*) and limnocorrals-containing Common Frogs (*Rana temporaria*) and Common Toads (*Bufo bufo*) in ponds at the Monks Wood Experimental Station in Huntingdon, England, exposed to diquat at a rate of 1 mg/L (Cooke 1977). No effects of the herbicide application were observed, except for the weight of tadpoles in the treated ponds that were lower than controls 4 days after treatment. The author found fewer algae and diatoms in the tadpoles' intestines, indicating that their food source was compromised as a result of the herbicide. After 18 and 32 days the tadpoles in the treatment limnocorrals were heavier than controls due to blooms of algae after the herbicide had dissipated. This result implies that while diquat caused an initial indirect negative effect, it also resulted in a longer-term benefit to frogs.

A third diquat field study was conducted in New Zealand, where Shortfin Eels (*Anguilla australis*) caged in limnocorrals in the Avon River, Christchurch, were exposed to 30 kg/ha diquat (resulting in a peak concentration of 3.51 mg/L), used to control the water weed, *Egeria densa*. Stress biomarkers, including hepatic mixed-function oxygenase, plasma lysosome, and vitellogenin, were observed and compared with controls caged upstream of the exposure reach 3 weeks after application (Tremblay 2004). No external stress symptoms such as fin rot or lesions were observed, and no differences were found between unexposed and exposed eels in body, liver, or spleen weight, lysozyme activity, plasma vitellogenin concentration, or mortality.

Mesocosm experiments of diquat also found no effect of diquat on aquatic organisms. Yeo (1967), for example, found that the application of diquat at concentrations up to 1 mg/L in mesocosms had no effect on fish, including Green Sunfish (*L. cyanellus*), Mosquitofish (*Gambusia affinis*), Smallmouth Bass (*Micropterus dolomieu*), or the freshwater clam, *Corbicula fluminea*, 30 days after application. As well, fingerling Rohu (*Labeo rohita*) in nursery tanks in Haryana,

[1]The concentration causing an "effect" in 50% of exposed individuals. This response in invertebrates is often based on immobility (i.e., the concentration causing 50% of individuals to be immobile) with no confirmation that the organism is dead or not.

[2]Dalton, R.L., Robinson, S.A., Sesin, V., Ben Othman, H., Boutin, C., Bartlett, A.J., and Pick, F.R. Unpublished data.

India, exposed to 1 mg/L diquat suffered no more mortality compared with controls (Yadava et al. 1993).

Overall, field studies examining the effects of direct applications of diquat to aquatic systems showed little, if any, effects on aquatic invertebrates, fish, and amphibians at initial concentrations that were far greater than many L(E)C_{50} values reported in lab studies. Although initial signs are promising with regards to the effects of the use of diquat on aquatic organisms, aquatic biota should be monitored before and after application to determine the potential effects.

Glyphosate

Glyphosate is a broad-spectrum systemic herbicide (Netherland 2014). This herbicide has been registered for aquatic use in the United States since 1977 (Netherland 2014), and is also registered for use in aquatic systems in Australia (Clements et al. 2014), New Zealand (Champion et al. 2011), the United Kingdom (HSE 2017), and various countries throughout the European Union and other countries worldwide, including Brazil, India, and Nigeria (Hussner et al. 2017 and references therein). Glyphosate is used to control shoreline vegetation and emergent weeds, such as Cattails (Netherland 2014; OMAFRA 2016; Hussner et al. 2017) and is one of two recent herbicides that have been granted emergency registration for use in Canadian waters to control the invasive *Phragmites* (e.g., OMNRF 2016), but it is not yet registered for general use.

Glyphosate does not significantly bioaccumulate, bioconcentrate, or biomagnify (Reinert and Rodgers 1987; Solomon and Thompson 2003; Siemering et al. 2008), leading the US EPA to conclude that glyphosate is practically nontoxic to nontarget organisms (US EPA 1993). Glyphosate is considered by several authorities (reviewed in Solomon and Thompson 2003) to have one of the lowest toxicities of all available herbicides; however, some formulations, cationic salt ions, and surfactants used in the application of glyphosate are more toxic than glyphosate itself (e.g., Brodman et al. 2010; reviewed in Harman 1995; Sinnott 2015). Glyphosate is typically applied to waterbodies in a wide range of doses up to about 4 mg/L (Pless 2005). Lab studies on aquatic organisms exposed to aquatic formulations of glyphosate have shown L(E)C_{50} values at concentrations well below field applications for aquatic invertebrates and fish (Table 1). No amphibian studies were found. Even the maximum LC_{50} of 6.4 mg/L documented for amphibians was slightly above the typical application rate of 4 mg/L. Lab LC_{50} studies thus imply that glyphosate could be deleterious to aquatic organisms, and that amphibians may be the most susceptible.

Considering glyphosate is the most common herbicide, field studies examining the effects of the direct application of this herbicide on aquatic organisms are not well documented in comparison to terrestrial applications. In the United States, no acute or chronic effects were found on the growth or survival of aquatic invertebrates or Rainbow Trout (*Oncorhynchus mykiss*) in situ after various applications of Rodeo (Dow AgroSciences LLC, Indianapolis, Indiana) to control various nuisance plant species including Cattails, Smooth Cordgrass (*S. alterniflora*), and Purple Loosestrife (*Lythrum salicaria*; Solberg and Higgins 1993; Henry et al. 1994; Gardner and Grue 1996; Simenstad et al. 1996). Linz and colleagues (1999) studied the response of aquatic invertebrates in North Dakota wetlands to the reduction in the coverage of Cattails 1 and 2 years post-treatment with Rodeo. The loss of Cattails resulted in increased abundance of Gastropoda (snails), Corixidae (diving beetles), Chironomidae (midge larvae), and general insect abundance when compared with control wetlands. There were no differences between the two treatments in the numbers of Cladocera (water fleas), Copepoda (small crustaceans), Crustacea, Hydracarina (water mites), Oligochaeta (aquatic worms), and Ostracoda (seed shrimp). Only Chaoboridae (phantom midges) were found to be more abundant in the control wetlands. The authors went on to conclude that the aquatic invertebrate community may be indirectly enhanced by the application of glyphosate due to the reduction of Cattails.

Approximately 2 mg/L Accord (Dow AgroSciences LLC, Indianapolis, Indiana), a glyphosate-based herbicide said to be less toxic to nontarget organisms than the more popular Roundup Custom (MONSANTO Company, St. Louis, Missouri) or Rodeo, and 1.2 mg/L of the surfactant Cide-KickII (Brewer International Inc., Vero Beach, Florida) was applied to constructed ponds, each containing different densities of Tiger Salamander (*Ambystoma tigrinum*) larvae, Northern Leopard Frog (*Lithobates pipiens*), Green Frog (*L. clamitans*), and American Toad (*Anaxyrus americanus*) tadpoles, and naturally occurring aquatic invertebrates (Brodman et al. 2010). The effect of Accord resulted in higher mortality in salamanders relative to controls. Salamanders also tended to spend more time in vegetation and in groups, their aggression decreased, and the proportion of microcrustaceans in their diets increased relative to controls. The addition of Accord generally increased Northern Leopard Frogs and American Toads survival and Northern Leopard Frog size relative to controls, presumably due to the reduction in the predatory salamanders. Green Frogs displayed reduced survival and number of metamorphizing individuals compared with controls. There was also a shift in the community structure of invertebrates. Microcrustaceans and malaocostracans were less abundant in the Accord-treated ponds relative to controls, whereas molluscs and benthic insects were more abundant. Benthic worms and pelagic insects did not differ. The authors concluded that, although there were some obvious effects of Accord and Cide-KickII, these effects were reduced compared to other glyphosate formulations that use ionic surfactants (Brodman et al. 2010).

Garnett and colleagues (1992) studied the effects of rates of 100 to 200 kg/ha glyphosate (a minimum concentration of approximately 5–10 mg/L, assuming a depth of 2 m) with a surfactant (wt.% nonyl-phenol-ethylene-oxide-condensate and 50 wt.% primary alcohol-ethylene-oxide-condensate) on invertebrate communities in three streams in England and Wales. In the Lindisfarne National Nature Reserve, Northumberland, the authors found significant and immediate (i.e., after one day) declines in the gastropod, *Hydrobia ulvae*, and the bivalve, *Macoma balthica*. Populations had recovered to similar or greater densities within a year post-treatment. The remaining species studied were unaffected by the herbicide application. In the Dee estuary, Cheshire, there was no effect of the application of the herbicide on nematode abundance. Finally, in the Dyfi Estuary, Dyfed, the nematode *C. volutator* abundance declined immediately post-treatment but had recovered within seven weeks after treatment.

Although not the same climate as Canada, the effects of 3.6 mg/L glyphosate on Jundiá (*Rhamdia quelen*) hormones, oocyte, and swim-up fry production were studied in earthen ponds in Brazil (Soso et al. 2007). Results indicated that glyphosate application causes negative impacts to catfish reproduction, altering egg viability and steroid profiles. Conversely, Adekoya (2002) and Olaleye and Akinyemiju (1996) studied fish abundance and pathology in Nigeria before and after treatment with 2.16 and 2.88 kg/ha glyphosate, respectively (a minimum concentration of approximately 0.11 and 0.14 mg/L, respectively, assuming a depth of 2 m), to control Water Hyacinth. Pathological instances decreased, and fish abundance increased after the addition of glyphosate. These results were attributed to the lack of the invasive plants, improving fish production.

Byrne and colleagues (2010) and Perschbacher and colleagues (1997) exposed mesocosms containing African Clawed Frog (*Xenopus laevis*) tadpoles and zooplankton, respectively, to glyphosate. The authors found no effect of glyphosate on either survival or body length of frogs or zooplankton abundance, concluding that glyphosate was not toxic to these organisms when used in typical field concentrations.

Field studies examining the effects of direct applications of glyphosate to aquatic systems generally displayed short-term or no effects on aquatic invertebrates and fish at or above realistic field exposure concentrations. Many studies suggest that the removal of the target weed has a beneficial response in these organisms (i.e., the potentially negative effects of the herbicide addition are outweighed by the positive effects of habitat change; e.g., Linz et al. 1999; Adekoya 2002). In accordance with the findings from lab studies, field studies examining the effects of glyphosate suggest that this herbicide can be toxic to certain high trophic level amphibians within the typical application range (e.g., Brodman et al. 2010). The surfactants and (or) other adjuvants used with glyphosate are often more toxic than glyphosate itself (e.g., Brodman et al. 2010) and could be driving this negative response. The surfactant used with aquatic herbicides should thus be chosen with caution and more studies into the toxicity of surfactants are required (e.g., reviewed in Pless 2005), and in particular, studies on amphibians, before glyphosate and glyphosate adjuvants can be justified for wide distribution and use in waterways.

Imazapyr

Imazapyr was registered for use in the United States in 2003 and in New Zealand in 2013 and has been used under emergency registration in Canada since 2013 (NZ EPA 2013; Netherland 2014; HTC 2016). This herbicide is a broad-spectrum systemic herbicide that is used in the control of many floating and emergent plants, such as Cattails, Japanese Knotweed (*Fallopia japonica*), *Phragmites*, and Purple Loosestrife (Netherland 2014; Hussner et al. 2017).

Imazapyr has a low propensity to bioconcentrate or bioaccumulate (Pless 2005). This herbicide also has a low potential for biomagnification and, consequently, has a low environmental impact to nontarget organisms (Neary et al. 1993). According to Fisher and colleagues (2003), imazapyr is practically nontoxic to birds, fish, invertebrates, and mammals. This herbicide is typically applied to waterbodies in rates of 0.18 to 0.55 mg/L (MDEP and MDAR 2012). All of the studies extracted from the US ECOTOX Database documented $L(E)C_{50}$ values well in excess of this typical application rate (Table 1); available studies are somewhat limited, particularly for amphibians. Regardless, based on these lab studies, imazapyr is unlikely to cause serious negative effects on nontarget aquatic organisms when used in ecologically relevant concentrations.

Only one field study was found in this review that documented the effects of aquatic formulations of imazapyr on aquatic organisms. In the single study, the benthic macroinvertebrate community was examined in experimental microcosms in a pine plantation near Gainsville, Florida (Fowlkes et al. 2003), prior to imazapyr being registered for aquatic use in the United States. The authors dosed each microcosm with 0.184, 1.84, and 18.4 mg/L imazapyr to simulate approximately 1, 10, and 100 times the expected environmental concentration following normal direct application, respectively. The authors examined the invertebrate community composition and the abundance and head-capsule deformities in chironomids. The lack of effects on all measured parameters led the authors to conclude that there was no effect of imazapyr, even at 100 times the expected environmental concentrations following direct application. With only a single field study that focused only on benthic macroinvertebrates, the use of imazapyr to control aquatic plants currently poses an unknown risk to many nontarget organisms in situ.

The various controlled toxicity tests provide some level of confidence that each of the three herbicides poses an understood and acceptable level of risk to nontarget organisms. Field studies provide a more realistic measure of effects, but are more time consuming than lab studies; invariably have a number of confounding factors that make it difficult to necessarily ascribe cause to effect; and can rarely address all of the possible combinations of receiving environment conditions, including species assemblages. It is unlikely that there will ever be enough field studies of any of the three herbicides to provide certainty that they are safe for general use in the real world without causing some level of change to some nontarget organisms. Monitoring the effects associated with controlled applications can be a means of accumulating information that may guide future uses of herbicides. Dubé and colleagues (2013) and others (e.g., Arciszewski et al. 2017) discussed how monitoring to test predictions based on a baseline of knowledge can be used to adaptively manage, or in this case use, herbicides. Of the three herbicides considered in this review, the data more strongly suggest that diquat could be used with the least effects to nontarget organisms in natural aquatic ecosystems. The use of diquat with monitoring of effects on nontarget organisms may be a justifiable alternative approach going forward.

Summary

Three herbicides (diquat, glyphosate, and imazapyr) have been, or are being, considered for more general use for controlling nuisance aquatic plants in Canada. Of the three herbicides, evidence suggests that diquat and glyphosate pose potentially negligible effects to nontarget aquatic organisms, including fish, invertebrates, and amphibians. In the case of glyphosate, one study found evidence for a decrease in abundances and altered behaviour of some amphibian species with a concurrent increase in abundances of other amphibian species at environmentally relevant concentrations (i.e., those that are used to control plants). There are no field data documenting the sensitivities of fish or amphibians to aquatic formulations of imazapyr. The surfactants used in many studies, may have driven negative results as the surfactants are often more toxic than the herbicide itself. Surfactants and other adjuvants added to increase the efficacy of the herbicides must thus be chosen carefully with consideration of the aquatic ecosystem that is being treated.

Despite field studies on diquat suggesting the product has benign effects, the field studies that have been undertaken have been somewhat limited in number and have not considered all of the possible receiving environment conditions (e.g., types of receivers, species assemblages, etc.) that are present in Canada. As a result, monitoring of the effects on nontarget species of any application of diquat (or either of the other two herbicides) is justifiable as a license requirement. Such monitoring could be valuable in furthering our understanding of the effects of herbicide treatments on the receiving environments (e.g., Arciszewski et al. 2017).

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