APPENDIX C: REVIEW OF ECOTOXICOLOGY AND ENVIRONMENTAL FATE OF FOUR HERBICIDES USED TO CONTROL AQUATIC WEEDS – NIWA
Review of ecotoxicology and environmental fate of four herbicides used to control aquatic weeds

Prepared for the Agrichemical Reassessment Group

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Executive summary

The Agrichemical Reassessment Group (ARG) is investigating the preparation and submission of an application to the New Zealand Environmental Protection Authority (EPA) for a modified reassessment of the herbicides metsulfuron methyl, haloxyfop methyl, imazapyr isopropylamine and triclopyr triethylamine (TEA) to allow their use within aquatic environments in order to manage plant pests. ARG group has engaged NIWA to prepare a summary document reviewing relevant literature, including unpublished reports, on the ecotoxicology and environmental fate of these herbicides.

Triclopyr TEA and imazapyr isopropylamine have very good environmental specifications and their registration for aquatic plant control in the USA indicates that these are suitable products for this aquatic use in New Zealand.

Metsulfuron methyl is of very low toxicity to animals, but is highly toxic at low concentrations to some non-target vascular plants and algae. Field studies have shown that these impacts are transitory. Although it is a relatively stable herbicide in water, dilution effects would soon reduce concentrations below toxic levels.

Haloxyfop-R-methyl is more toxic than the other herbicides, although most information, especially from New Zealand comes from a more toxic earlier formulation of haloxyfop – the ethoxyethyl ester. To date, extensive use of haloxyfop to control spartina and Manchurian wild rice has provided no evidence of long-term damage to the ecology of sites where this product has been applied.

Compared to the threats posed by the weed species targeted for management using these products; their continued use, with restrictions on their use, is seen as appropriate.
1 Introduction

The Agrichemical Reassessment Group (ARG) is investigating the preparation and submission of an application to the New Zealand Environmental Protection Authority (EPA) for a modified reassessment of the herbicides metsulfuron methyl, haloxyfop methyl, imazapyr isopropylamine and triclopyr triethylamine (TEA) to allow their use within aquatic environments in order to manage plant pest infestations. ARG is comprised of the Ministry for Primary Industries (MPI), Department of Conservation (DOC), Land Information New Zealand (LINZ), 12 Regional Councils and Mighty River Power (MRP). This group has engaged NIWA to prepare a summary document reviewing relevant literature, including unpublished reports, on the ecotoxicology and environmental fate of these herbicides.

This report details the available information for each of the four herbicides and discusses the likely contamination that would occur from their proposed use and potential for off-target impacts.
2 Review Methodology

Information on the ecotoxicology and environmental fate was sourced from Specimen Labels and Material Safety Data Sheets for each product, websites collating environmental information (e.g., EXTOXNET), published scientific literature and unpublished New Zealand studies (see Section 5).

The review focussed on organisms likely to be impacted by the application of these herbicides, with common test organisms including aquatic birds (mallard duck- *Anas platyrhynchos*), fish (rainbow trout-*Oncorhynchus mykiss* and bluegill sunfish-*Lepomis macrochirrus*), water flea (*Daphnia magna* and *D. pulex*) and a range of freshwater and marine algae. Several New Zealand studies have assessed the impacts on native species. Mammalian toxicity has also been included in the review as a proxy for potential impacts on human health, with rats being the commonest test organism.

As herbicides, the products reviewed are designed to be toxic to a range of plant species. This review focusses on toxicity to non-target aquatic and wetland plants (predominantly angiosperms) likely to be impacted by the proposed use of these herbicides.

This review comprehensively covers all the available information on toxicity to aquatic organisms and environmental fate in aquatic habitats.
3 Herbicides

3.1 Metsulfuron methyl

Metsulfuron methyl was first used in New Zealand for aquatic weed control under resource consent by Environment Waikato in 1994 for control of alligator weed (*Alternanthera philoxeroides*) (Champion 2008). There are currently a number of consents permitting the use of this herbicide within New Zealand. Maximum concentration of herbicide permitted under these consents is currently 15 g/100 L of spray mix. van Oosterhout (2007) reports that several permits for aquatic use of metsulfuron methyl have been issued for alligator weed control in some non-potable waterways in Victoria and New South Wales.

Metsulfuron methyl is currently available under the trade names Agmax Met 600, Agpro Meturon®, Agronica Metsulfuron, Associate® 600 WDG, Donaghy’s Brushweed Kill Met600, Eradicate 600, Escort®, Matrix® WDG, Mustang®, Prism, Synergy™ Met600 and Zeal™, all in the form of a water dispersed granule at a concentration of 600 g/kg of the active ingredient. Answer® has 200 g/kg active ingredient and is in the form of a water soluble granule (New Zealand Novachem Manual 2012).

3.1.1 Toxicology

The label for all formulations of metsulfuron methyl states that those products are ecotoxic, being very toxic to aquatic organisms (New Zealand Novachem Manual 2012).

At the rate proposed within the reevaluation application the concentration of metsulfuron methyl in the spray mix applied to plants is 21 mg/L (or mg/kg).

The following literature has been used to generate the summary below: Thompson et al. (1993 a & b); EXTOXNET (1993); Champion & Chisnall (1994); Peterson et al. (1994); Fahl et al. (1995); Champion et al. (1997); Fairchild et al. (1997); Nystrom & Blanck (1998); Nystrom et al. (1999); Boutin et al. (2000); Ray & Wells 2000; Faust et al. (2003); Wendt-Rasch et al. (2003); Klotzback & Durkin (2004); Cedergreen et al. (2004; 2005); Ma et al. (2006).

**Mammalian toxicity**

**Very low toxicity**

Acute oral toxicity that causes mortality (Lethal Dose) in half of the test animals (rats) (LD$_{50}$) >5000 mg/kg.

Metsulfuron methyl is broken down quickly and eliminated from the body. In tests with radiolabeled metsulfuron-methyl in rats, the excretion half-lives ranged from 9 to 16 hours and 23 to 29 hours for rats administered low and high doses, respectively.

Metsulfuron methyl is an irritant to eyes and skin in its solid form (water dispersed granule), with risks posed to the chemical applicator when making the spray mix.

**Avian toxicity**

**Very low toxicity**

Acute oral toxicity - mallard (LD$_{50}$) > 5000 mg/kg.
Aquatic animal toxicity

Very low toxicity

96-hour (Lethal Concentration) LC$_{50}$ – rainbow trout and bluegill sunfish (North American fish found in warmer parts of US) > 150 mg/L.

48-hour LC$_{50}$ – *Daphnia magna* (cladoceran crustacean) > 150 mg/L.

A 21-day life-cycle test with *Daphnia magna* also exhibited very low toxicity. The non-observable effect level (NOEL) for survival and reproduction was >150 mg/L.

Field trials using up metsulfuron methyl concentrations up to 1 mg/L to a Canadian lake showed no impact on zooplankton species including rotifers, cladocera and copepod (another group of planktonic crustaceans) (Thompson et al. 1993a).

Champion et al. (1997) found no toxicity to longfin or shortfin eelers (*Anguilla dieffenbachii* and *A. australis*) at rates well above herbicidal concentrations used. Caged eels, inanga (*Galaxias maculatus*), freshwater shrimp (*Paratya curvirostris*) held upstream and downstream of treated areas on the Waikato River showed no mortality during and after the treatment and there was no difference in the number or diversity of other fish or invertebrate species captured in the treated areas (Champion & Chisnall 1994).

Non-target aquatic plant toxicity

Selectively very toxic

Metsulfuron methyl is currently used to selectively control a range of emergent (plants with foliage above the water level) plants e.g., alligator weed, yellow flag iris and arrowhead, but does not appear to affect grasses and sedges at rates herbicidal to target species (Champion 1994; Ray & Wells 2000; Chiconella et al. 2004). Boutin et al. (2000) found non-target wetland species *Bidens cernua*, *Mimulus ringens* and *Echinochloa crus-galli* were impacted by treatment with herbicide rates at 10% the recommended rate, also with lesser damage at 1% of recommended rate. These rates were derived as typical rates that vegetation adjacent to target vegetation would receive.

Submerged and free-floating plant susceptibility was tested by Cedergreen et al. (2004; 2005) with Petersen et al. (1994) also testing the free-floating *Lemma minor*. Of the species tested only two *Lemma* species and *Ceratophyllum demersum* were deleteriously impacted out of a total of 12 species tested. Cedergreen et al. (2005) also tested the impact of a pulsed dose of metsulfuron methyl, with a four day check on plant growth before recovery to pre-treatment levels. Conversely, Wendt-Rasch et al. (2003) found concentrations of 1 μg/L (0.001 mg/L) metsulfuron methyl checked the root growth of *Elodea canadensis* and *Myriophyllum spicatum* after 14 days exposure to this concentration. No plant death was noted at levels up to 20 μg/L tested in this study.

Thus submerged plants are unlikely to be impacted by metsulfuron methyl discharge into water associated with the uses proposed. Champion & Chisnall (1994) found no evidence of damage to non-target vegetation in the Waikato Delta.
Algae

Selectively very toxic

Ecotoxicology studies using a range of algal species have found toxicity ranging from moderate to highly toxic (Thompson et al. (1993b); Peterson et al. (1994); Fahl et al. (1995); Fairchild et al. (1997); Nystrom & Blanck (1998); Nystrom et al. (1999); Faust et al. (2003); Ma et al. (2006).

The most extensive screening of algal species was undertaken by Nystrom et al. (1999) who tested 20 freshwater and 20 marine algae belonging to eight different phyla including cyanobacteria (blue-green algae). There was a variation of six orders of magnitude (one million times) in calculated LC50, with values ranging from 120.2 mg/L to <375.7 ng/L (0.0003757 mg/L). The most sensitive species were cyanobacteria, with the most sensitive species Anabaena flos-aquae. All other toxicities measured by other researchers fall within this range. Fahl et al. (1995) found toxicity of metsulfuron methyl to Chlorella fusca varied by a factor of up to 1000 times with an Effective Concentration causing 50% inhibition of growth (EC50) at pH 6.5 of 1.2 mg/L, decreasing (becoming more toxic) with lower pH.

Field observations of phytoplankton community response to metsulfuron methyl range from slight reduction in cyanobacteria numbers at concentrations of 1 mg/L, with rapid recovery to pre-treatment levels and no discernible change of other species (Thompson et al. 1993b).

3.1.2 Persistence in aquatic habitats

Thompson et al. (1992) noted a persistence of metsulfuron methyl in the surface waters of a Canadian boreal forest lake with the time taken for 50% of the product to dissipate (DT50) >84 days when at a concentration of 1 mg/L or 29.1 days when at a concentration of 10 μg/L. EXTOXNET (1993) states that metsulfuron methyl is stable to hydrolysis at neutral or alkaline pH, but has a half-life of 33 days at pH 5. Wang et al. (2011) monitored the dissipation of metsulfuron methyl in an artificial pond. After 5 days 50% of the compound had dissipated, falling to 15.6% after 30 days and 0.7% after 90 days.

Champion et al. (1997) collected drain water immediately after marginal alligator weed plants had been treated with metsulfuron methyl. A maximum concentration measured from samples taken immediately downstream of the treated area was 0.18 mg/L, equivalent to 1/350 the concentration of the herbicide mixture applied to plants. In a larger drain a maximum concentration measured was 12.6 μg/L. No residue of metsulfuron methyl was detected one day, one week or one month after treatment. Water samples taken at the time of treatment were kept in an aquarium with sub-samples analysed every week. Concentration of metsulfuron methyl remained approximately stable for a 90 day period.

Metsulfuron methyl is rapidly taken up by plants at the roots and on foliage. The chemical is translocated throughout the plant, but is not persistent. It is broken down to non-herbicidal products in tolerant plants.

3.1.3 Summary and discussion

Metsulfuron methyl is not registered for use in situations where contamination of aquatic environments may occur. This herbicide has very low toxicity to animals, including a range of aquatic species. Many aquatic plants including sedges, grasses and many submerged
species are tolerant to the effects of metsulfuron methyl at the concentrations it is applied in the field.

However, metsulfuron methyl is herbicidal at very low concentrations to susceptible plants including algae and in static waters with no dilution effects it is a stable compound except in low pH waters.

The use of this herbicide to manage problem aquatic weeds such as alligator weed has been undertaken under various resource consents in the upper North Island. Current maximum rates of metsulfuron methyl applied to marginal aquatic weeds would equate to 84 g/ha assuming a water rate of 400 L spray mix/ha. If the maximum area to be treated were to be 100 m², then the total amount of herbicide used would equate to 800 mg of metsulfuron methyl. With the maximum contamination rate (1/350) measured by Champion et al. (1997) it is unlikely that total amounts of contamination resulting from careful application of metsulfuron methyl herbicide would exceed 1 mg. Dilution effects would rapidly reduce the concentration of metsulfuron methyl especially in large flowing water bodies.

3.2 Haloxyfop-R-methyl

Haloxyfop was first used for aquatic weed control in the Bay of Plenty in 1991 for control of spartina (Spartina alterniflora) in Ohwa Harbour (Shaw and Gosling 1995). At that time the only formulation of haloxyfop available (as the trade name Gallant™) was haloxyfop ethoxyethyl. Control of spartina (both S. alterniflora and S. anglica) now occurs in most regions of New Zealand. Turner & Hewitt (1997) designed a monitoring programme for DOC to meet monitoring requirements for the Waikato Region resource consent. Haloxyfop has also been used to manage other aquatic grasses including Manchurian wild rice (Zizania latifolia) and saltwater paspalum (Paspalum vaginatum) in Waikato and other regions in the North Island. There are currently a number of consents permitting the use of this herbicide within Waikato Region. Newer formulations of Gallant and all currently available herbicides with haloxyfop have haloxyfop-R-methyl as the active ingredient.

Haloxyfop-R-methyl is currently available under the trade names Agpro haloxyfop 100, Hurricane®, Ignite™, Scorp® EC and Valiant, all in the form of an emulsifiable concentrate at a concentration of 100 g/L of the active ingredient. Gallant™ Ultra has 520 g/L active ingredient also in the form of an emulsifiable concentrate (New Zealand Novachem Manual 2012).

3.2.1 Toxicology

The label for Gallant™ Ultra states that the product is ecotoxic, being very toxic to aquatic organisms. Other formulations are listed as harmful to terrestrial vertebrates, but not ecotoxic (New Zealand Novachem Manual 2012).

At the rate permitted by the resource consent the concentration of haloxyfop-R-methyl in the spray mix applied to plants is 750 mg/L (or mg/kg).

The following literature has been used to generate the summary below: Roberts (1992); EXTOXNET (1995); Shaw & Gosling (1995); Roper et al. (1996); Shaw (1999); Champion et al. (2001); Ma et al. (2006); Champion & Hofstra (2010).
Mammalian toxicity

Moderate toxicity

Acute oral toxicity of haloxyfop-R-methyl to rats LD₅₀ 393 mg/kg.

Chronic effects do occur at lower concentrations with teratogenic and reproductive effects reported for haloxyfop ethoxyethyl in rats at 10–50 mg/kg body weight and kidney damage reported in adult rats at doses of 100 mg/kg/day (EXTOXNET 1995). No evidence of haloxyfop being carcinogenic to rats or mice. In rats, haloxyfop-ethoxyethyl undergoes metabolism to haloxyfop which is excreted in faeces and urine (EXTOXNET 1995).

Avian toxicity

Very low toxicity

Acute oral toxicity - mallard LD₅₀ > 5000 mg/kg.

Aquatic animal toxicity

Variable toxicity

Haloxyfop-methyl is practically non-toxic to fish.

96-hour LC₆₀ of haloxyfop acid –

- fathead minnow > 1000 mg/L.
- bluegill sunfish 548 mg/L
- rainbow trout > 800 mg/L

48-hour LC₅₀ – Daphnia magna 96.4 mg/L.

However, the previous formulation available (haloxyfop-ethoxyethyl) is moderately to highly toxic to fish. The LC₅₀ (96 hour) is 0.54 mg/l for fathead minnows, 0.28 mg/l for bluegill sunfish, and 1.8 mg/l for rainbow trout. The 48-hour LC₅₀ for Daphnia magna is 4.6 mg/L.

Field trials monitoring the impacts of spraying Spartina using haloxyfop-ethoxyethyl (Roberts 1992) showed no impacts on caged organisms including inanga, eel, cockabullies and shrimp, with no observed impact on the gastropods Amphibola crenata, Potamopyrgus estuarinus and the crab Helice crassa.

Roper et al. (1996) carried out ecotoxicology tests using haloxyfop-ethoxyethyl using the marine bivalve Macomona littorea and the amphipod Chaetocorophium cf. lucasia, using 96 hour acute toxicity and 10 day survival tests. The bivalve was subjected to short-term burial tests recording the number of animals that had buried into sediment after 5 to 30 minutes. Amphipods were killed at 10 mg/L or higher concentrations but survived below this and 50% were killed at the rate the herbicide was applied to control spartina (900 g/ha). All bivalves survived the 96 hour test at the concentration applied to control spartina. However, this rate inhibited the ability of ~90% of M. littorea tested to bury within a 30 minute period.

Champion et al. (2001) carried out ecotoxicology tests on elvers, inanga and freshwater shrimp using haloxyfop. These tests found the product was highly toxic to elvers and inanga with 96 hour LC₅₀ values of 0.42 and 0.52 6 μg/L respectively. These values far exceed values reported in EXTOXNET (1995).
Non-target aquatic plant toxicity

Selectively very toxic to grass species

Hal oxyfop-R-methyl is currently used to selectively control a range of emergent grasses, and does not appear to affect non-grasses including sedges, rushes and other monocotyledons and dicotyledons at rates herbicidal to target grass species (Champion 1998).

Field experience of the author with haloxyfop-R-methyl used to control spartina and Manchurian wild rice have shown mangrove (Avicennia marina subsp. australasica), flax (Phormium tenax), Machaerina (Bau mea) articulata and Bolboschoenus fluviatilis all to be tolerant of this product at rates applied to the target species.

Algae

Possibly very toxic

Ma et al. (2006) compared the toxicity of 40 herbicides to the green alga (Chlorophyta) Pseudokirchneriella subcapitata. They reported a 96-hour LC50 of 1.08 mg/L (compared with 24.70 mg/L for metsulfuron methyl and 5.56 mg/L for glyphosate). Champion et al. (2001) found much higher toxicity for the freshwater alga Pseudokirchneriella subcapitata and the marine species Minutocellus polymorpha of 43 and 8.3 ng/L respectively.

3.2.2 Persistence in aquatic habitats

EXTOXNET (1995) report a half-life of hal oxyfop in water of 33 days in water of pH 5, reducing with increased pH (5 days at pH 7 and several hours at pH 9). Degradation is by hydrolysis.

A maximum concentration of hal oxyfop-ethoxyethyl measured by Roper et al. (1996) from samples taken within the treated area was 4.3 µg/L, equivalent to 65 times lower than toxicity (LC50) of the most sensitive fish (bluegill sunfish), with 31 µg/L of the primary degradation product hal oxyfop acid being the maximum recorded concentration. The acid was approximately 1000 x less toxic than hal oxyfop-ethoxyethyl.

3.2.3 Summary and discussion

Hal oxyfop-R-methyl is not registered for use in situations where contamination of aquatic environments may occur. This herbicide has variable toxicity to animals, including a range of aquatic species, from being practically non-toxic to mallards and fish to being moderately toxic to mammals. There were no data for hal oxyfop-R-methyl on aquatic invertebrates, with values obtained for either hal oxyfop-ethoxyethyl and hal oxyfop acid used, with hal oxyfop-ethoxyethyl found to be strongly toxic. However, hal oxyfop-ethoxyethyl appears to be more ecotoxic than the R-methyl formulation based on EXTOXNET (1995) data.

All non-grasses tested including aquatic plants are tolerant to the effects of hal oxyfop-R-methyl at the concentrations it is applied in the field. Some algae appeared to be extremely sensitive to Gallant. Hal oxyfop is broken down by hydrolysis in water with degradation most rapid at alkaline pH.

The use of this herbicide to manage problem aquatic weeds such as spartina has been undertaken under various resource consents throughout New Zealand for more than 20 years, with consents also issued for control of Manchurian wild rice in 2001. Current
maximum rates of haloxyfop-R-methyl applied to marginal aquatic weeds would equate to 750 g/ha assuming a water rate of 400 L spray mix/ha. If the maximum area to be treated were to be 100 m², then the total amount of herbicide used would equate to 7.5 g of haloxyfop-R-methyl. Dilution effects would rapidly reduce the concentration of haloxyfop-R-methyl especially in large flowing water bodies.

Roper et al. (1996) state that use of haloxyfop-ethoxyethyl for control of spartina is likely to cause some toxic effects on benthic organisms, especially where spray ponds after application. They state that spraying may cause temporary decline in the density of some species, but toxicity would not persist and benthic communities would recover. They suggest a 5-day ban on shellfish harvesting within 500 m of the sprayed area. Concentrations of haloxyfop rapidly fell below toxic levels by tidal flushing in this study. Since that time haloxyfop, with the newer formulation being haloxyfop-R-methyl, is regularly applied to manage this species, with Shaw (1999) stating that off-target impacts are at an acceptable level, with negative impacts minimised or avoided by timing of application and careful application to target plants.

### 3.3 Imazapyr isopropylamine

Imazapyr isopropylamine was first registered for use in New Zealand as the chemical name Arsenal, used for total vegetation control. In the USA the same product was also registered for aquatic use under the name Habitat®. Under this label a range of emergent and floating plants are able to be managed by this product including the following plants problematic in New Zealand: marshwort, fringed waterlily, yellow waterlily, water hyacinth, alligator weed, arrowhead, sagittaria, waterlily, primrose willow, spartina, giant reed, Japanese knotweed, phragmites, purple loosestrife and willows (SePRO 2011), following the Reregistration Eligibility Decision Document for Imazapyr by US EPA (2006).

Arsenal is no longer available in New Zealand but imazapyr isopropylamine is available under the trade name UniMaz® 250SL, an aqueous solution containing 250 mg/L imazapyr isopropylamine (United Phosphorus 2010). It was registered for use by ERMA in November 2009 (ERMANZ 2009). Under Section 4.21.5 (Additional controls) UNIMAZ 250SL shall not be applied onto or into water.

#### 3.3.1 Toxicology

The label for UniMaz® 250SL states that this product is ecotoxic, being very toxic to aquatic organisms (New Zealand Novachem Manual 2012).

Current use for the management of phragmites is at a concentration of 1.5 kg/ha.

**Mammalian toxicity**

**Very low toxicity**

Acute oral toxicity of imazapyr isopropylamine to rats LD₅₀ >5000 mg/kg. There is no evidence of effect at the highest rates tested for acute or chronic toxicity (US EPA 2006).
Avian toxicity

Very low toxicity

Acute oral toxicity - mallard LD$_{50}$ > 5000 mg/kg.

Aquatic animal and non-vascular plants toxicity

Very low toxicity

Imazapyr isopropylamine is practically non-toxic to fish, aquatic invertebrates and non-vascular plants.

96-hour LC$_{50}$ of imazapyr isopropylamine –
  - bluegill sunfish > 1000 mg/L.
  - rainbow trout > 800 mg/L

48-hour LC$_{50}$ – *Daphnia magna* 614 mg/L.

7-day EC$_{50}$ – *Pseudokirchneriella subcapitata* 11.5 mg/L.

Non-target aquatic plant toxicity

Selectively very toxic

Imazapyr isopropylamine is highly toxic to a range of monocotyledons and dicotyledons, with seedling emergence and vegetative vigour severely impacted (US EPA 2006). Included in sensitive species aquatic free-floating *Lemna gibba* with a 48-hour EC$_{50}$ of 24 μg/L (Fisher et al. 2003). Patten (2003) directly sprayed marine eelgrass (*Zostera japonica*) plants at the same rate as that used to control Spartina and these were killed, re-establishing 12 months after treatment. However, if they were sprayed while there was a film of water still covering them, then plants were unaffected.

3.3.2 Persistence in aquatic habitats

EXTOXNET (1995) report a half-life of imazapyr isopropylamine in water of 2.5–5.3 days. Degradation is by photolysis.

Patten (2003) sampled water in an area of spartina treated with imazapyr isopropylamine. The maximum level found in water after application was 3.4 mg/L, with no residue detectible after 40 hours.

3.3.3 Summary and discussion

Imazapyr isopropylamine is not registered for use in situations where contamination of aquatic environments may occur in New Zealand. However, this herbicide has been approved for aquatic use by the USEPA and has been successfully used to manage a range of pest plants there. This herbicide is practically non-toxic to mammals, mallards, fish, aquatic invertebrates and algae, but is toxic to a wide range of plant species.

Current maximum rates of imazapyr isopropylamine applied to marginal aquatic weeds would equate to 1.5 kg/ha. If the maximum area to be treated were to be 100 m$^2$, then the total amount of herbicide used would equate to 15 g of imazapyr isopropylamine. Dilution effects
would rapidly reduce the concentration of imazapyr isopropylamine especially in large flowing water bodies.

3.4 Triclopyr triethylamine (TEA)

Triclopyr TEA was registered for use in New Zealand for use in wetlands under the chemical name Garlon™ 360. In the USA the same product is also registered for aquatic use under the name Renovate®, where it is used to control a range of emergent and floating weeds and the submerged Eurasian water milfoil (Myriophyllum spicatum). The Garlon™ 360 label (Dow AgroSciences 2007) lists alligator weed, parrot's feather and willows as species controlled by this product. Additionally, Renovate® includes alder, blackberry, hawthorn, water hyacinth, primrose willow, waterlily and purple loosestrife (SePRO 2008).

Garlon™ 360 is an aqueous solution containing 444 g/L triclopyr TEA.

Currently Garlon™ 360 cannot be applied directly to un-impounded rivers or streams, salt water bays or estuaries, where run-off may flow onto agricultural land, canals or ditches used to transport irrigation water or water for human consumption. There are no restrictions for livestock watering, recreational water use or swimming.

3.4.1 Toxicology

The label for Garlon™ 360 states that this product is ecotoxic, being highly toxic to aquatic plants (New Zealand Novachem Manual 2012).

Current maximum use rate for the management of alligator weed is at a concentration of 7.92 kg/ha.

Mammalian toxicity

Low toxicity

Acute oral toxicity of triclopyr TEA to rats LD$_{50}$ 2574 mg/kg. There is little evidence of effect at the highest rates tested for chronic toxicity (EXTOXNET 1996).

Avian toxicity

Very low toxicity

Acute oral toxicity - mallard LD$_{50}$ > 10000 mg/kg.

Aquatic animal toxicity

Very low to low toxicity

Triclopyr TEA is practically non-toxic to fish and aquatic invertebrates

96-hour LC$_{50}$ of triclopyr TEA – bluegill sunfish 891 mg/L
rainbow trout 552 mg/L
fathead minnow 120 -101 mg/L (Mayes et al. 1984)

48-hour LC$_{50}$ – Daphnia magna 110 mg/L (Gersich et al. 1984).
96-hour LC$_{50}$ – crayfish (Procambarus clarkii) >103 mg/L (Petty et al. 2003)

Champion & Hofstra (2001) found no mortality of caged eels and inanga held below a wetland areas treated for the control of parrot’s feather using triclopyr TEA, endothall and dichlofenil.

**Non-target aquatic plant toxicity**

**Selectively very toxic**

Triclopyr TEA is highly toxic to a range of predominantly dicotyledonous plants, with auxin-like impacts on growth regulation.

Champion et al. (2008a & b) and Hofstra et al. (2006) found susceptible plants included a wide range of dicotyledonous plants, but many monocotyledons especially grasses, some sedges and rushes and the gymnosperm kahikatea (Dacrycarpus dacrydioides) were tolerant of rates herbicidal to target plants in a pot trial. Field trials (Champion et al. 2011) resulted in the decrease in cover of dicotyledons, apart from an increase in annual species, whose germination would have been stimulated by increased light due to death of target weeds. Other perennial species recovered within one year after treatment. As with the pot trials grasses and sedges were unharmed and increased in abundance.

**Algae**

**Moderately toxic**

7-day EC$_{50}$ - *Anabaena flos-aquae* 5.97 mg/L

5-day EC$_{50}$ - *Skeletonema costatum* 11 mg/L

**3.4.2 Persistence in aquatic habitats**

EXTOXNET (1995) report a half-life of triclopyr TEA in water of 2.8 -14.1 hours. Petty et al. (2003) found half-life of triclopyr TEA in water of 0.5 -7.5 days.

Degradation is predominantly by photolysis.

**3.4.3 Summary and discussion**

Triclopyr TEA is registered for use in situations where contamination of aquatic environments may occur in New Zealand, but there are restrictions on its use in many of the situations that weeds targeted for control may occur. This herbicide has been approved for a much wider range of aquatic use by the USEPA, including its use as a submerged herbicide. Fortunately the submerged target species Eurasian milfoil does not occur in New Zealand, but control of emergent weeds such as parrot’s feather is required in flowing water systems. This herbicide is practically non-toxic to mallards, fish, aquatic invertebrates and only moderately toxic to algae, but is selectively toxic to a wide range of dicotyledonous plant species.

Current maximum rates of triclopyr TEA applied to marginal aquatic weeds would equate to 7.92 kg/ha. If the maximum area to be treated were to be 100 m$^2$, then the total amount of herbicide used would equate to 79.2 g of triclopyr TEA. Dilution effects would rapidly reduce the concentration especially in large flowing water bodies.
Petty et al. (2003) conclude that triclopyr TEA is rapidly degraded and, combined with its excellent ecotoxicological profile and selectivity of control for exotic weedy species will make this product a valuable tool for restoring and managing aquatic ecosystems.
4 Recommendations

Triclopyr TEA and imazapyr isopropylamine have very good environmental specifications and their registration for aquatic plant control in the USA indicates that these are suitable products for this aquatic use in New Zealand.

Metsulfuron methyl is of very low toxicity to animals, but is highly toxic at low concentrations to some non-target vascular plants and algae. Field studies have shown that these impacts are transitory. Although it is a relatively stable herbicide in water, dilution effects would soon reduce concentrations below toxic levels.

Haloxifop-R-methyl is more toxic than the other herbicides, although most information, especially from New Zealand comes from a more toxic earlier formulation of haloxifop – haloxifop ethoxyethyl. To date, extensive use of haloxifop to control spartina and Manchurian wild rice has provided no evidence of long-term damage to the ecology of sites where this product has been applied.

Compared to the threats posed by the weed species targeted for management using these products; their continued use, with current restrictions outlined in the reassessment proposal, is seen as appropriate.
5 References


