Environment Waikato Technical Report 2006/03

Review of Diquat Reports of Relevance to Iwi Values in Lake Karapiro

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ISSN: 1172-4005

December 2005

Document #: 1051810

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NIWA Client Report: HAM2005-136
December 2005

NIWA Project: EVW06207

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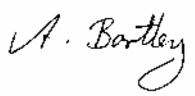
Formatting checked



Executive Summary

Environment Waikato contracted NIWA to review several investigative reports dealing with the impacts of the aquatic herbicide diquat in the environment when used for aquatic weed control. The purpose of the review was to determine whether the results from these reports were reliable and consistent with other information on the use of diquat. Comment was also requested on the impact of this particular control method on iwi values, particularly the eel fishery.

Three references were supplied by Environment Waikato for this review, including Tremblay (2001), Landward Management (2005), and a pesticide information profile on diquat from the EXTOXNET website (http://extoxnet.orst.edu/). Additional references were also reviewed.

Reglone® product undiluted contains 20% of the active ingredient, diquat dibromide. Reglone® is diluted 100,000 times by water to attain the concentration required for control of waterweeds (1 $mg.l^{-1}$ of diquat dibromide). This is equal to only 1 drop of Reglone® product in 10 litres of water. Diquat treatment of aquatic weed beds first began in the Rotorua Lakes in 1960 and has been used there regularly for 45 years. The concentration of diquat in water rapidly declines after application as a result of dispersion, plant uptake and adsorption to organic and inorganic (negatively charged) particles. When applied to weed beds in an open waterbody the concentration of diquat often falls below detection limits within 1 hour or so of being applied. No evidence exists for toxic accumulations of diquat residues in bottom sediments following repeated usage. Diquat concentrate is a toxic substance, but at diluted rates for control of nuisance submerged weeds it is so diluted that it is less toxic than other common household products such as chlorine as used in swimming pools.

A review of reports addressing the impact of diquat usage in New Zealand found no evidence of toxicity and no significant changes in sensitive physiological biochemical markers in short-finned eels. Other field studies have shown no significant changes in mussels, shrimps, inunga, bullies, and koura presence inside and outside areas treated for weed control.

Targeted control of nuisance weed beds can provide habitat diversity by minimising specific problems arising from excessive weed growth in target areas, while maintaining the benefits of vegetation presence in uncontrolled areas. Extensive, uncontrolled dense weed beds can be more detrimental to the mauri through the decline in water quality and associated biota than from any potential impacts arising from diquat usage for the control weed beds. With respect to Waikato iwi values such as the mauri and freshwater kaimoana for consistency with the iwi overall strategy for the awa it would be advised that weed management be viewed in terms of a long-term management goal or strategy for the awa. This type of strategy should consider protecting and enhancing iwi values in conjunction with wider stakeholder activities and will require further discussion and development.

1. Introduction

NIWA was asked to review several investigative reports that deal with the impacts of the aquatic herbicide diquat when used for aquatic weed control on the environment. The purpose of the review was to determine whether the results from these reports were reliable and consistent with other information on the use of this herbicide. Comment was also requested on the impact of this particular control method on iwi values, and in particular the eel fishery.

Environment Waikato in conjunction with Waipa District Council, LINZ, Mighty River Power and Waikato iwi are seeking solutions to address the aquatic weed problems in Lake Karapiro in so far as they may potentially impact on a number of national and international sporting events. For example, Rowing New Zealand is aiming to host the Rowing World Cup; however this bid would be jeopardised by the aquatic plant *Ceratophyllum demersum* (hornwort) interfering the boating course if it is not effectively controlled. Hornwort has no roots and is readily dislodged to become entrained with the water flow. Drifting plant material becomes readily entangled with submerged obstacles such as drowned trees and mooring lines and continues to grow provided there is sufficient light.

To prevent hornwort drift from impacting on the Lake Karapiro rowing course it is proposed that a combination of control methods will be required, including mechanical interventions (such as weed booms and mechanical harvesting) combined with some targeted control using the aquatic herbicide diquat. A Consent for diquat herbicide use is proposed as part of the total package of control options. Iwi groups with an interest in the lake have expressed some concern about the discharge of herbicide to the lake environment. A number of reports have been undertaken within New Zealand on the impact of diquat on the environment and this information is reviewed.

2. Methods

Three references were supplied by Environment Waikato for this review, including Tremblay (2001), Landward Management (2005), and a pesticide information profile on diquat from the EXTOXNET website (http://extoxnet.orst.edu/)

Additional references have also been included in this review, including Clayton (1986 & 2004), Wells & Clayton (1996), and HortResearch (2001).

3. Results and Discussion

3.1 General

Diquat (technical name of the salt - diquat dibromide) is the active ingredient in Reglone®, and it is used in New Zealand for both agricultural operations and in water for lake-weed control. Diquat treatment of aquatic weed beds first began in the Rotorua Lakes in 1960 and has been used there regularly now for 45 years. When diquat comes into contact with the green parts of nuisance aquatic weeds (leaves and stems) it is rapidly absorbed producing peroxide that acts like bleach, desiccating plant tissue and disrupting cell membranes. The concentration of diquat in water rapidly declines after application as a result of dispersion, plant uptake and adsorption to organic and inorganic (negatively charged) particles. When applied to weed beds in an open waterbody the concentration of diquat often falls below detection limits within 1 hour or so of being applied. Adsorbed diquat has no residual toxicity, is not biologically active, and is degraded slowly by microbial organisms within sediments.

Diquat is a selective herbicide that controls most unwanted target weed species in freshwaters, including elodea, egeria, lagarosiphon and hornwort. Many key native plant species that are important in New Zealand lakes, such as *Chara* and *Nitella* species, are not affected by diquat.

3.2 Waikato iwi values for Waikato awa

The concerns raised by Waikato with respect to weed control in the lake are strongly linked to the mauri of Waikato Awa. Linked closely to mauri is the status of freshwater kaimoana in the awa. Species such as tuna, kakahi and koura are taonga and negative impact on these species causes a decline in the overall mauri of the system. These generic concerns apply to freshwater bodies throughout New Zealand, while specific iwi values for the Waikato awa require further clarification as part of the development of a longer term strategy to establish a system of sustainable management for aquatic vegetation in the Waikato River and hydro lakes. Further cultural input will be needed to develop a collective understanding of the Waikato values and to identify the benefits of various weed control options most suitable for the longer term.

3.3 Toxicity of Diquat

Reglone® product in its concentrated form contains 20% of the active ingredient diquat dibromide. Reglone® is classified under HSNO (Hazardous Substances & New Organisms Act 1996) on a scale of risk that places it one class less toxic than nicotine and two classes lower than caffeine. Reglone® is diluted 100,000 times with water to attain the concentration required for control of water weeds (1 $mg.l^{-1}$ of diquat dibromide salt). The application rate permitted (based on both the product label instructions) does not exceed 30 litres per hectare even in deep water. The target concentration of 1 $mg.l^{-1}$ (1 ppm) is achieved with this application rate when mixed with 0.5m depth of water, so lesser concentrations are usually achieved. At 1 $mg.l^{-1}$, this is equal to only 1 drop of Reglone® product in 10 litres of water. Alternatively this can be compared to walking only 1m along a 100 km journey. The safety of this concentration means that regulations in the USA allow direct water contact by swimmers immediately after treatment. In New Zealand there is a 24-hour post-treatment prohibition period for swimming. This is a very conservative safety precaution (to ensure no contact with diquat), which can be misinterpreted by the public.

A comparison of diquat to other well known substances in everyday use shows a much higher amount of diquat is required to achieve a toxic effect on test organisms compared to caffeine or nicotine. A more relevant comparison can be made with chlorine, which is toxic at lower levels, but is used at similar rates in swimming pools as diquat is in lakes.

3.4 Toxicity to fish

A key consideration in this report is to assess the impact of diquat used for weed control on iwi values such as mauri and freshwater kaimoana, and in particular the eel fishery. Before addressing the potential risk of diquat on eels it is worth considering what information has been published on fish species known to be more sensitive to pollution and chemical contaminants in general.

Trout are one of the most sensitive fish species known and are used as an indicator species for fish in general. For adult trout the LC_{50} (96 hrs exposure) is 12.2 – 37.4 mg L^{-1} and for juveniles the chronic (21 day) LC_{50} is 5.8 mg L^{-1} (diquat dibromide). For most other fish diquat must exceed 20 mg L^{-1} diquat dibromide for lengthy periods for mortality. Diquat is also used to treat bacterial gill infections in fish at concentrations up to 28 mg L^{-1} for 1 hour or more. Note the key factors for toxicity are concentration and length of time of exposure. Short exposure times of an hour or less are typical when diquat is applied to most lakes. In the case of Lake Karapiro this means that there would be no risk to trout from use of diquat for weed control. If native trout (kaoro) were ever exposed to diquat at the low rates used to control weeds then it is expected that their sensitivity would be in the same order of magnitude as for rainbow trout, especially given the greater than ten fold safety margin in the concentration and exposure times needed to affect rainbow trout compared to controlling weeds. Kaoro have not been recorded from Lake Karapiro on account of elver migratory barriers, so the eel fishery is the key issue for consideration in this report.

A particularly cogent study on the effects of diquat on eels was undertaken by Tremblay (2001 & 2004) from the Centre for Environmental Toxicology (CENTOX) within Landcare Research at Lincoln. The Christchurch City Council (CCC) contracted Landcare Research to evaluate the potential of diquat to cause adverse effects to the short-finned eel (*Anguilla australis*). This initiative followed a series of public consultations by the CCC, concerned iwi and other interest groups that identified objectors concerns to be potential for toxicity to fish and bioaccumulation of herbicide chemicals or by-products in fish tissues. In order to address these concerns the study by Tremblay (2001) used proven in situ biomonitoring methods to measure the effects of diquat treatment on a range of specific physiological responses in eels caged upstream and downstream from a diquat treated section of the Avon River in Christchurch. What makes this study very relevant is the fact that a series of sensitive physiological responses or biomarkers were measured, including hepatic mixed-function oxygenase, plasma lysozyme, and vitellogenin. The use of a variety of specific and non-specific biomarkers is able to provide a functional measure of exposure to stressors, which would typically indicate a response to stress at even lower levels than the standard NOAEL (No Observed Adverse Effect Level) and of course is a far more sensitive response measure than standard LC_{50} measurements used to determine the concentration of a test product that will kill (Lethal Concentration) 50% of a test organism. Following diquat application to the Avon River for weed control, diquat dibromide concentration was no longer detectable after 1 hour of application. It is common for diquat to decline rapidly to undetectable levels (<0.0001 $mg.l^{-1}$) after application on account of dilution and dispersion, plant uptake, adsorption to inorganic matter suspended in the water, and adsorption onto bottom sediments. Overall, the results of the Avon River testing showed that diquat treatment caused no observable signs of acute toxicity in the short-finned eel and did not significantly alter biomarker responses (Tremblay 2004). Eels are generally regarded as a relatively hardy fish species compared to the likes of rainbow trout, which are deliberately used in toxicity testing on account of their recognised sensitivity to a wide range of toxicants. Based on the absence of any physiological biomarker responses in short-finned eels it would be reasonable to conclude that a similar or identical response would be expected for long-finned eels.

Another study on potential diquat impacts on eels was carried in Lake Benmore (Landward Management New Zealand 2005). The area treated with diquat was quite large (c. 50 ha) and at a treatment rate of 30 litres Reglone per hectare, this equated to c. 1500 litres diquat, which was applied by helicopter to the newly invasive *Lagarosiphon* weed bed at the Ahuriri Delta. A representative of Ngai Tahu assisted with this study by capturing eels from suitable locations within the treated area. Two pre-spray eel samples were collected from the Lake Benmore Ahuriri Delta in November 2004 and a further two eel samples 10 weeks later in January 2005. The samples were analysed by Hill Laboratories and the results found no detectable trace (<0.02 mg kg^{-1}) of diquat present in any of the eel samples either before or after the diquat treatment.

3.5 Toxicity to shellfish

Freshwater mussels (kakahi) are commonly used around the world for environmental monitoring because as bottom filter feeders they are vulnerable to accumulation of contaminants. The New Zealand freshwater mussel (*Hyridella menziesi*) is prolific in Lake Rotorua with up to 550 m^{-2} recorded in quadrant samples. In 1994-95 a study was carried out on the impacts of weeds beds and diquat on the freshwater mussel in Lake Rotorua (Wells & Clayton 1996). Diquat had been used on a regular basis in this lake for over 30 years by this stage. A comparison of mussel size and densities beneath diquat treated and untreated weed beds showed no evidence of diquat impact. The size range of mussels between treated and untreated sites was similar which indicated that diquat was not affecting recruitment. Evidence was further supported by an acute toxicity test on adult mussels subjected to a one-off diquat addition to their tank at between 5-10 times the rates to control weed beds (i.e., 10 mg.l^{-1}). The mussels were monitored for the next 2 months and showed 100% survival.

3.6 Toxicity to other biota

Some of the earliest diquat toxicity experiments in the 1960s focused on a wide variety of freshwater biota. No measurable effect was noted on most life forms when diquat was used at herbicidal rates, although subtle effects were observed on small planktonic crustaceans such as cladocerans. Immobilisation concentrations (IC_{50}) were noted on *Daphnia* at 7.1 mg l^{-1} and inhibition of adult growth development at 1 mg l^{-1} diquat (studies quoted in Wilson & Bond 1969), suggesting the potential for some impact on invertebrates of importance to fish. The most sensitive known aquatic organisms to the diquat cation are amphipods (minute crustaceans <5mm long), which have an LC_{50} (96 hrs) of 0.05 mg l^{-1}. However, using a 96 hour LC_{50} on aquatic organisms (such as trout and amphipods) is inappropriate when compared to the half life of diquat in lake water.

However, despite these concerns the use of diquat in the field has demonstrated rapid dispersion and adsorption with exponential loss from treated areas and little evidence to suggest likely diquat toxicity to organisms in the field.

The first comprehensive study undertaken in New Zealand to look at the potential non-target effects of diquat use was carried out in the Rotorua Lakes in the 1970s after diquat had been in use on a regular basis for over 10 years (Graham 1976). Graham found no evidence of detrimental effect on trout and no significant changes in plankton or benthic organisms. He concluded that continued use of diquat was acceptable on account of these findings and fate of diquat loss through sedimentation, adsorption and degradation.

Recent ecological studies have been carried out in Blenheim waterways to assess the impact of diquat use for drain weed control. Two separate waterways were sampled above and below the area targeted for diquat treatment with samples collected prior to spraying and again a few days after treatment. There were no significant changes observed in any of the biota sampled, including shrimps, inanga, bullies, and koura (Wells 2005, in prep). Diquat in water was not detectable ($<0.002\ mg.l^{-1}$) in one waterway after 1 hour, and in the other it was $0.012\ mg.l^{-1}$ after 5 hours.

3.7 Diquat residue

Diquat is rapidly adsorbed on to inorganic matter and is then biologically inactive with no residual toxicity. Adsorbed diquat is degraded slowly by microbial organisms but concern has been expressed over the long term use of diquat and the potential for build up of adsorbed diquat in sediment.

In March 2000, NIWA staff collected sediment samples from five lakes with quite different histories of exposure to diquat usage. At this time, diquat has been used regularly over a period of 40 years for lake weed control in the Rotorua Lakes. Surface sediment samples (10 mm deep cores) were from a water depth of 3 metres in Lakes Rotoiti and Rotorua in areas known to have been regularly and recently sprayed for weed control. Sediment samples were also collected from a lake with less regular diquat application (Lake Okataina), a lake with historical diquat treatment in the 1970s and 1980s (Lake Rotoroa, Hamilton) and a lake not previously treated with diquat. The diversity of lakes was chosen to represent a variety of lake types in terms of size, sediment qualities, lake trophic status and treatment histories. The samples were analysed by HortResearch and all samples had no detectable diquat residue. Deactivated adsorbed diquat residue is extremely difficult to measure accurately using standard analytical procedures and experienced operators. This has led to some inconsistency in results between laboratories, however the key point is that even if any diquat residue is present, it is completely deactivated and of no biological or ecological consequence.

3.8 Impact from uncontrolled weed beds

Although native aquatic vegetation is preferable in terms of ecological properties, the presence of abundant invasive species may be still better than no submerged vegetation. Targeted control of nuisance weed beds can be an appropriate strategy for providing habitat diversity by maintaining the benefits of vegetation presence in uncontrolled areas, while minimising specific problems arising from excessive weed growth in target areas. Where invasive dense weed beds are extensive, uncontrolled dense weed beds can be more detrimental to the mauri through the decline in water quality and associated biota than from any potential impacts arising from diquat usage for the control weed beds. Data loggers placed inside tall dense submerged weed beds have shown quite remarkable fluctuations in dissolved oxygen and pH levels. For example, this was vividly demonstrated in Lake Omapere in Northland in February 2001 after the invasive weed *Egeria densa* had invaded right across this large shallow lake. Deoxygenation of bottom waters occurred as a result of surface-reaching beds of egeria preventing movement of oxygen through the water column and this event killed many freshwater mussels on the lake bottom (Champion & Burns 2001).

Tall dense weed beds can also result in habitat modification caused by the accumulation of flocculent organic matter in the sediments beneath the weed beds. This lowers the density of sediment and can cause freshwater mussel shells to sink below the sediment surface and suffocate. For example, this has been observed in several of the Rotorua lakes such as Rotoehu and Rotokakahi (pers. obs.) and is likely to explain the demise in mussel populations in most of the Waikato lakes since the advent of *Egeria* and hornwort.

4. Conclusions

Diquat concentrate is a toxic substance, but at diluted rates for control of nuisance submerged weeds it is so diluted that it is less toxic than other common household products such as chlorine as used in swimming pools.

Diquat is considered non-toxic to fish at rates required to kill aquatic weeds, and field experiments on caged eels have confirmed no acute toxicity or physiological response could be measured when exposed to diquat field treatments. Similarly, diquat is considered non-toxic to the New Zealand freshwater mussel at the rates required to kill aquatic weeds. Other field studies have also shown no significant changes in shrimps, inunga, bullies, and koura inside and outside areas treated for weed control. The potential for diquat to affect small planktonic crustaceans given extended exposures has been demonstrated under laboratory testing, however in natural waterbodies this impact has not been observed.

The application of diquat in Karapiro can be viewed as non-harmful to key taonga species (Table 1) and will assist in the protection of the overall mauri of the awa and is a tool that can be used in wider strategy developed for weed control. With respect to Waikato iwi values such as the mauri and freshwater kaimoana for consistency with the iwi overall strategy for the awa it would be advised that weed management be viewed in terms of a long-term management goal or strategy for the awa. This type of strategy should consider protecting and enhancing iwi values in conjunction with wider stakeholder activities and will require further discussion and development.

5. References

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Table 1: Summary of iwi values, issues and discussion

Value	Issue	Discussion
Mauri	That the application of diquat will undermine the mauri of the awa	Uncontrolled dense weed beds can be more detrimental to the mauri through the decline in water quality and associated biota than from any potential impacts arising from diquat usage for the control weed beds.
Freshwater Kaimoana	That the application of diquat will negatively impact on the quantity and quality of key taonga species.	Diquat is considered non-toxic to fish at rates required to kill aquatic weeds, and field experiments on caged eels have confirmed no acute toxicity or physiological response could be measured when exposed to diquat field treatments. Similarly, diquat is considered non-toxic to the New Zealand freshwater mussel at the rates required to kill aquatic weeds. Other field studies have also shown no significant changes in shrimps, inunga, bullies, and koura inside and outside areas treated for weed control. The potential for diquat to affect small planktonic crustaceans has been demonstrated under laboratory ecotoxicity testing, however the mitigating influences of natural waterbodies has meant that this impact has not been observed under natural field conditions.