Overview of potential piscicides and molluscicides for controlling aquatic pest species in New Zealand

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Cover: Spraying Rotenone to kill pest fish in Nelson-Marlborough Conservancy.

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ABSTRACT

Introductions of exotic freshwater species have resulted in at least 21 species of fish and several species of snails becoming established in New Zealand, some of which pose a significant threat to freshwater biodiversity. We undertook a literature and internet search of piscicides (chemicals toxic to fish) and molluscicides (chemicals toxic to snails) for use in New Zealand freshwater environments. Piscicides have been in use for many years in Asia, North America and Europe for aquaculture and conservation purposes. Niclosamide is used in Asia and Africa to eradicate snails. The options for eradication fall into two categories: specific compounds, which offer some control over which species are targeted; and general treatments intended to kill all aquatic life in an area. Specific compounds assessed were: antimycin, AQUI-S, saponins (including teaseed cake) and niclosamide (Bayer 73). General treatments assessed were deoxygenation of the water (using dry ice, sodium sulphite, sugar), and the addition of lime, ammonia or chlorine. Although rotenone is the main piscicide used internationally for eradicating and controlling freshwater pest fishes, it is not assessed in this report as its suitability for use in New Zealand has been previously reviewed. The advantages and disadvantages of each alternative are summarised and, to further assist managers, a decision-support tool is included.

Keywords: pest fish, eradication, piscidicide, molluscicide, freshwater.

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1. Introduction

Both legal and illegal introductions of exotic fishes have occurred since the 1860s in New Zealand, resulting in 21 species of freshwater fishes becoming established. Some of these fish species pose a significant threat to freshwater biodiversity (Dean 2003). Various options for minimising the impacts of these pest fish species have been proposed, including containment at existing sites, management as an acclimatised species and eradication using piscicides (e.g. Champion et al. 2002; Chadderton 2003; Dean 2003). The last option, chemical control, yields its best results when a combination of physical, chemical and biological management techniques are used, based on a sound understanding of the pest species and its interaction with the ecosystem concerned (Champion et al. 2002).

There are many different circumstances under which fish eradication may be warranted, and the following practical approach has been recommended.

> 'Regardless of the methods employed, fish stress and time to death must be minimized as much as practical, and death ensured. Human safety (with regard to chemical usage and food safety) and environmental safety should also be taken into consideration. In addition, compliance with local authority and government regulations must be ensured for all operations. Appropriate trained personnel and experts intimately involved with the specific situation and current regulations should be part of the decision-making process, and implementation of the operation.' (Yanong et al. 2007)

At least 26 species of introduced freshwater invertebrates are established in New Zealand (Sandlant 2002). Winterbourn (1973) reported five introduced mollusc species, which were probably introduced with acquarium stock into New Zealand. Recently, a thiarid snail (*Melanoides tuberculata*) native to the Middle East and East Africa has been recoreded in a geothermally influenced stream, most likely the result of one or more releases from tropical aquaria (Duggan 2002). Establishment of cosmopolitian mollusc species such as *M. tuberculata* have the potential to change habitat conditions and to adversely impact native species populations (Duggan 2007).

Within society, interpretative differences exist between stake-holders, regulators, Iwi and practitioners over the actions and terminology involved with fishery management. In addition, laboratory scenarios (that involve small closed systems, simple manipulations and treatments, and controlled environmental conditions) differ in significant ways from field scenarios (that involve large water bodies and hundreds or thousands of fishes, sometimes of large and/or variable sizes, and are affected by weather and other uncontrollable elements). Decision-makers must be aware of and understand the different perceptions held and the practices associated with each scenario. In many instances, operations will be based on accepted standard practices, and decisions should include the input of those with experience in the specific field or circumstance (Yanong et al. 2007).

In New Zealand, the introduction of substances into an aquatic environment cannot be undertaken without statutory compliance with existing national, regional and local legislation and regulations. The use of substances for control of aquatic pest species in New Zealand is regulated by the Agricultural Compounds[1] and Veterinary Medicines Act 1997. Substances must be registered with the Agricultural Compounds & Veterinary Medicines (ACVM) Group. Substances must also comply with requirements of the Hazardous Substances and New Organisms (HSNO) Act 1996, and be approved by the Environmental Risk Management Authority (ERMA) for use in New Zealand. In addition, the Resource Management Act (RMA) 1991 requires resource consents to be obtained from regional councils before the discharge of substances into the aquatic environment.

Rotenone is the main piscicide used internationally for eradicating and controlling pest fishes in freshwaters (Rowe 2003). Chemical eradication using rotenone has been used for fisheries management in Canada and the USA since the 1930s (Finlayson et al. 2002), and also in Australia for about 45 years (Rayner & Creese 2006). The use of rotenone has been very limited in New Zealand (Ling 2003; Rayner & Creese 2006). Both whole lake dosing and poisoned-bait treatments have been undertaken. In 1981, Lake Parkinson (Waiuku) was treated to eradicate all fishes, including grass carp (*Ctenopharyngodon idella*) following their introduction to remove nuisance water plants (Ling 2003). A bait form of rotenone, developed in the USA (Prentox®), was used in Lake Waingata to remove grass carp in 1999 (Rowe 1999). A review of the toxicity and use of rotenone for fisheries management in New Zealand has been previously undertaken (Ling 2003).

Although eradication of alien molluscs from New Zealand freshwater environments has not been a focus of attention by waterway managers, considerable effort has been applied to the eradication of molluscs internationally. For instance, the eradication of schistosome-bearing snails in Asia and Africa has been used to as a measure to control schistosomiasis in humans (e.g. Tshounwou et al. 1991).

The Department of Conservation (DOC) contracted NIWA to undertake a literature search and an initial screening of alternate chemical methods to the use of rotenone for the eradication of fishes (i.e. piscicides) and snails (i.e. molluscicides) for use in New Zealand freshwater environments as stated in the overview of the contract below:

> '8. Overview
>
> This study will provide a search and initial screening of alternative chemical methods for eradication of fish (termed 'piscicides') and snails (termed 'molluscicides') to the use of rotenone. In particular the review will focus on chemical methods with minimal environmental impact (e.g. deoxygenation via sodium sulphite) and methods that will be useful in small bodies of water. The critical review will include advantages and disadvantages of each method, practicality of delivery systems, efficacy of action, chemical monitoring ability, environmental persistence, effects on non-target species (including humans),

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[1] An agricultural compound is defined in the Act as:
' … any substance, mixture of substances, or biological compound, used or intended for use in the direct management of plants and animals, or to be applied to the land, place, or water on or in which the plants and animals are managed, for the purposes of—
(a) Managing or eradicating pests, including vertebrate pests; or….
…and any substance, mixture of substances, or biological compound declared to be an agricultural compound for the purposes of this Act by Order in Council made under subsection (2).'

> costs and possible social issues relevant to New Zealand. A summary data sheet summarising these factors will be produced for each chemical, together with a decision-support matrix to assist in method selection relative to the scale and nature of the environmental problem. The review will assist DOC in undertaking a risk-based decision approach to the choice of chemical methods for early intervention for control of invasive and pest species. The review will not be an exhaustive examination of existing data on each chemical. The final report will provide supporting documentation to accompany applications under the Resource Management Act (RMA) for use of rotenone (see review by Ling 2003), or other methods recommended in this review.'

The compounds or techniques reviewed are: antimycin, AQUI-S, saponins (including teaseed cake), niclosamide (Bayer 73®), deoxygenation (using dry ice, sodium sulphite, sugar or micro-organisms), lime, ammonia and chlorine. Rotenone is not included because it has already been reviewed (Ling 2003) and DOC is currently using this compound.

The lampricide 3-trifluoromethyl-4-nitrophenol (TFM) was initially included in the assessment, but subsequently removed at the request of DOC as there are currently no exotic species of lamprey in New Zealand. In the USA, it is primarily used as a lampricide to control larval lampreys entering the Great Lakes (GLFC 2000). TFM is more toxic to lampreys than other fish species, and is used approximately every 4 years, allowing populations of non-target species (especially shorter-lived invertebrates) to recover sufficiently between treatments (GLFC 2000).

The treatment methods described can be broadly divided into species-specific treatments and more general eradication treatments, which affect all species. General eradication treatments may be useful in some situations, for example in small enclosed water bodies, whereas more specific treatments will be appropriate in larger systems.

The report includes a description of each compound or technique, identification information, available formulations, application rates, availability and registration in New Zealand, cost comparisons (based on 2007 prices), human health issues, environmental fate, target and non-target species, and the advantages and disadvantages of each approach. We have not attempted to provide an in-depth ecotoxicological analysis of each compound. We conclude the report with a comparison of the compounds (including rotenone) to identify the best option(s) for different pest species in different freshwater environments.

2. Methods

We conducted a literature and Internet search for each compound or technique using the following search engines, websites and databases in 2003 and 2007: Google, Amazon, Bayer Corp, Aquatic Science and Fisheries Abstracts, PAN Pesticides Database (PAN North America 2003), ACVM Database (ACVM Group 2003), US Environmental Protection Agency ACQUIRE Ecotox Database (USEPA 2003) and EXTOXNET (EXTOXNET 2003).

Since each treatment has a different application rate, we have made the costs comparable by basing our estimates on treating a hypothetical pond which is $4000\,m^2$ (1 acre) in size and 2 m deep (total volume = $8000\,m^3$), even though some treatments are not ideally suited for pond use. Prices are correct as of September 2007.

The report is organised into separate chapters for each treatment option, in order to provide a profile of each chemical.

If the chemical is included in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC 2000), we report the recommended 'trigger values', which are the chemical concentrations that should not be exceeded in receiving waters for a long-term (chronic) discharge. Comparison of the exposure concentrations to the ANZECC (2000) trigger values provides a conservative indication of the potential for adverse effects on non-target species. However, site-specific evaluations may be desirable for many situations where short-term (acute) exposures occur.

Chemical Abstract Service Numbers (CAS Numbers) are reported for some chemicals. CAS Numbers are unique identifiers for individual chemicals, used to avoid the confusion of systematic chemical nomenclature and common chemical names.

The Animal Welfare Act 1999 requires that manipulations involving live animals are subject to a Code of Ethical Conduct (CEC) approved by the Minister of Agriculture. A manipulation is defined as an interference with the normal physiological, behavioural or anatomical integrity of the animal by deliberately:

> '(a) Subjecting it to a procedure which is unusual or abnormal when compared with that to which animals of that type would be subjected under normal management or practice and which involves—
>
> (i) Exposing the animal to any parasite, micro-organism, drug, chemical, biological product, radiation, electrical stimulation, or environmental condition; or
>
> (ii) Enforced activity, restraint, nutrition, or surgical intervention; or
>
> (b) Depriving the animal of usual care'

However, there are exceptions, significantly for animals in the wild:

> '(d) The hunting or killing of any animal in a wild state by a method that is not an experimental method'.

Therefore, the use of established procedures and formulations for eradication of pest fishes in the wild would not require a CEC to comply with the Act. However, we recommend that fishes are killed in such a manner that they do not suffer unreasonable or unnecessary pain and distress.

3. Specific treatment—antimycin

3.1 COMPOUND

Antimycin.

3.2 SYNONYMS/FORMULATIONS

Antimycin is not just one compound; it has four major and four minor components. The manufacture of antimycin includes fermentation and refinement processes that affect its composition and quality. Some of the terms used to refer to antimycin are listed below:

- Antimycin A
- Antimycin A_1
- Antimycin A_3
- 3-methylbutanoic acid 3-[[3-(formylamino)-2-hydroxybenzoyl]amino]-8-hexyl -2,6-dimethyl-4,9-dioxo-1,5-dioxonan-7-yl ester
- Isovaleric acid, 8-ester with 3-formamido-N-(7-hexyl-8-hydroxy-4,9-dimethyl-2,6-dioxo-1,5-dioxonan-3-yl) salicylamide
- Blastmycin

Fintrol is the formulation of antimycin currently registered and available in North America, sold in 240-mL volumes of a 23% concentrate (weight/weight) in acetone, with 240 mL of diluent (acetone-surfactant mix). The weight of active ingredient is very low because of the high potency of the compound. The concentrate and diluent are mixed just prior to application. The co-solvent and surfactants in the diluent are diethylphthalate and nonoxynol-9.

3.3 ACTIVE INGREDIENT

Antimycin A_1 (CAS Number: 642-15-9) or Antimycin A_3 (CAS Number: 522-70-3).

3.4 MECHANISM

Antimycin is a cellular respiration inhibitor and is used in cellular physiology studies for its specific action as an electron transport inhibitor, specifically for mitochondrial complex III (Eighmy et al. 1991; Doeller et al. 1999). Antimycin is particularly toxic to scaled fishes, is less toxic to channel catfish (*Ictalurus punctatus*), and has low toxicity to other aquatic organisms (Finlayson et al. 2002). Juvenile life stages are more susceptible than adult fishes to antimycin (Finlayson et al. 2002). Antimycin toxicity is affected by water quality (e.g. pH, temperature) (Marking 1992).

3.5 USES

In a survey of antimycin use in the USA and Canada, government fisheries agencies were estimated to use about one-quarter of the antimycin sold annually since 1996 (Finlayson et al. 2002). Further, the average total usage of antimycin was estimated to be 5 kg/year (Finlayson et al. 2002). The greatest use of antimycin by these agencies occurs in the western and midwestern regions of the USA to restore threatened or endangered native trout populations (Finlayson et al. 2002).

Between 1996 and 2002, the remaining c. 75% of antimycin purchased in the USA and Canada was used by private aquaculture facilities (Finlayson et al. 2002). Since catfish are less sensitive to antimycin than some scaled fishes or invertebrates, catfish farmers use antimycin to remove unwanted scaled fishes and invertebrates from large production ponds (Finlayson et al. 2002).

Antimycin has also been used to selectively remove smaller individuals of a species, e.g. bluegills (*Lepomis macrochirus*) (Schneider & Lockwood 2002). Bottom-release (granular) formulations (0.25% active ingredient) might have some use in the selective treatment of benthic fish species, e.g. ruffe (*Gymnocephalus cernuus*) (Dawson et al. 1998).

Precise dosing of antimycin A has been used in the removal of green sunfish (*Lepomis cyanellus*) from channel catfish in live-haul tanks after transport and prior to the stocking of production ponds (Lloyd 1987). The fish are treated for 15 min at doses from 25 to 200 µg/L, depending on ambient pH and temperature. Based on LC_{50} values[2], sunfish are 45 times more sensitive to antimycin than catfish (Finlayson et al. 2002), and would die at concentrations well below the concentrations causing catfish mortality. This removal of green sunfish prior to the stocking of the production ponds resulted in substantial cost savings as it avoided expensive whole pond treatments at a later date (Lloyd 1987).

In North America, antimycin is most effective in small streams, shallow ponds and alpine lakes, whereas rotenone is used in large rivers and deep lakes (Finlayson et al. 2000).

3.6 APPLICATION RATES

Antimycin is sold commercially as Fintrol. One unit of Fintrol is sufficient to treat 1 hectare-metre (= 10 000 m^3) at the recommended application rate (5 µg/L) but, as mentioned, its effectiveness depends on water temperature and pH. Based on a conversion factor of 0.044 to convert units of Fintrol to kilograms of antimycin (Finlayson et al. 2002), this equates to 0.044 kg (4×10^7 µg) of antimycin.

In terms of the effect of pH on its toxicity to fishes, from pH 6.5 to 8.5 toxicity gradually decreases, and at higher pH values (8.5–9.5), toxicity is markedly reduced (Marking 1975; Marking 1992). Water hardness has very little effect on antimycin toxicity (Lee et al. 1971).

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[2] LC_{50} is the concentration that kills 50% of the individuals exposed to a treatment for a defined exposure time.

In cold water, toxicity may be reduced. Antimycin was very effective at killing larval sea lampreys (*Petromyzon marinus*) in the Great Lakes region: an application rate of 150 g/ha resulted in over 90% mortality, whilst at 75 g/ha, mortality was 90% in warm water, but reduced to 66% in cold water (Gilderhus 1979; Marking 1992).

The 96-h LC_{50} for the freshwater teleost *Lebistes reticulatus* is 0.0014 mg/L (Gupta et al. 1984) and ranges from 0.57 to 1.00 µg/L for four species of carp: the common carp (*Cyprinus carpio*), grass carp (*Ctenopharyngodon idella*), bighead carp (*Aristichthyes nobilis*) and silver carp (*Hypophthalmichthyes molitrix*) (Marking & Bills 1981).The 96-h LC_{50} for the black eel and glass eel stages of the American eel (*Anguilla rostrata*) in a static exposure, with warm water (22°C) of moderate hardness and alkalinity is 0.28 mg/L and 0.09 mg/L, respectively (Hinton & Eversole 1979).

An antimycin concentration < 1.0 µg/L causes 100% mortality in trout and char (Family: Salmonidae) (Finlayson et al. 2002). Freshwater catfish (Family: Ictaluridae) are less sensitive, requiring concentrations of 25–200 µg/L to cause 100% mortality. Most minnows (Family: Cyprinidae) and sunfish (Family: Centrarchidae) suffer mortality at antimycin concentrations of 5–10 µg/L (Finlayson et al. 2002).

Antimycin can be removed from water by using activated carbon in a water-treatment system (Dawson et al. 1976). Deactivation can be undertaken using potassium permanganate (USEPA 2007).

3.7 COST

Fintrol is currently not available in New Zealand, and quoted prices are from suppliers in the USA. For prices in New Zealand currency, the current exchange rate would apply. Freight charges from the USA would also apply. Two suppliers and prices for 2005 are:

Aquabiotics Corporation:	US$400/Unit Fintrol or US$400/0.044 kg Fintrol
Southern Aquaculture Supply:	US$500/16 oz (3 lb) Fintrol = one 'unit'

Treatment of the hypothetical 8000-m^3 pond with an application of 20 µg/L to eradicate catfish would require 0.16 kg antimycin (4 units of Fintrol) and cost US$1600 (plus freighting costs). Based on an currency exchange rate of 0.7907[3], the cost would be a minimum of NZ$2024.

3.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

Not registered for use as an agricultural compound in New Zealand. Reregistered for use in the USA in 2007 (USEPA 2007).

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[3] www.ird.govt.nz/calculators/keyword/overseascurrencies/ (viewed 29 November 2007).

3.9 SOURCE

Antimycin is a compound produced by the filamentous bacterium *Streptomyces grieseus* (Finlayson et al. 2002).

Manufacturer:	Aquabiotics Corporation, Nick and Mary Romeo, 3386 Commercial Avenue, Northbrook, Illinois, USA 60062. Ph: 001 206 842 1708.
Distributor:	Southern Aquaculture Supply Inc, 931 Saint Mary's Street, Lake Village, Arkansas, USA 71653. Ph: 001 870 265 3584; Fax: 001 870 265 4146.

3.10 TARGET

Antimycin is more toxic to scaled fishes such as trout and char (Family: Salmonidae) than catfish (Family: Ictaluridae), minnows (Family: Cyprinidae) and sunfish (Family: Centrarchidae). Fry and fingerlings have a greater sensitivity than juveniles and adult fishes (Finlayson et al. 2002).

Antimycin-impregnated baits have been used to target common carp (Rach et al. 1994). The bait pellets consisted of fish meal, a binding agent, antimycin and water. Doses of 10 mg antimycin/g bait caused low (19%) to high (74%) mortalities in fish feeding voluntarily on 50 g of the toxic bait in each of three earthen ponds. The baits are best used in conjunction with other management techniques and should be distributed only when feeding aggregations of the target species and low numbers of non-target species are present (Rach et al. 1994). As far as we know, antimycin bait formulations are not available in New Zealand or North America at the moment.

Antimycin has been used successfully to eradicate brook trout (*Salvelinus fontinalis*) from a tributary of Yellowstone Lake, USA (Gresswell 1991). The treatment covered the drainage of the tributary and included a 23.6-ha lagoon. Post-treatment surveys revealed that spawning migrations of the desirable Yellowstone cutthroat trout (*Oncorhynchus clarkii bouveri*) could still occur. Treatment success appeared to be a result of accurate estimation of toxin dispersal and good application techniques (Gresswell 1991).

Antimycin has also been used to eradicate or reduce pest fish populations in Scottish lochs and streams (e.g. Morrison 1979). The piscicide has generally been found to be less toxic to bottom-dwelling invertebrates than to fishes (Finlayson et al. 2002).

Antimycin treatment was used to remove gambusia (*Gambusia affinis*), a non-native mosquitofish, from a brook in Arizona because they were competing with the endangered local species, the Gila topminnow (*Poeciliopsis occidentialis*). Even though the gambusia appeared to have been completely removed, and the replacement populations of topminnows rapidly expanded, the gambusia re-entered the system several months later (Meffe 1983).

Antimycin A was more toxic to the freshwater snail *Viviparus bengalensis* than was the molluscicide Bayer 73® or the lampricide TFM (Gupta & Durve 1983). In some situations it could be an advantage to have access to a product that acts as a molluscicide as well as a piscicide.

Antimycin toxicity to fathead minnows (*Pimephales promelas*) was not significantly affected by the presence of Canadian waterweed (*Elodea canadiensis*), but was significantly reduced in the presence of high concentrations of suspended bentonite clay (Gilderhus 1982).

3.11 NON-TARGET

No information was located on the sensitivity New Zealand native fish species to antimycin. The sensitivity of Australian galaxiids and other native fishes to antimycin has also not been determined (Roberts & Tilzey 1996). At concentrations used to control pest fish populations in the USA, antimycin has minimal effects on other aquatic organisms such as invertebrates (Finlayson et al. 2002). In addition, Chandler & Marking (1979) found that antimycin A was less toxic to the Asiatic clam (*Corbicula manilensis*) than fishes. Fishes and other aquatic organisms have been found to be more sensitive to antimycin than mammals and birds, owing to the chemical's rapid absorption into the bloodstream from the water across the gills (Finlayson et al. 2002).

For terrestrial animals, antimycin has been found to be highly toxic to mice, rats, rabbits, guinea pigs, dogs and lambs (Finlayson et al. 2002).

3.12 HUMAN HEALTH

There are few data available on the toxicity to humans (USEPA 2007). Finlayson et al. (2002) identified conjunctivitis as a possible consequence when applying the treatment, and recommended the use of safety glasses when handling the product. In the absence of any definitive human health studies, the USEPA (2007) recommends the following procedures be implemented:

- Prohibition of fish harvesting from treated areas for 12 months
- Closure of drinking water intakes until antimycin A levels are below 0.015 µg/L
- Prohibition of public access to the treated area for 7 days after application
- Deactivation of antimycin in outflows with potassium permanganate
- Wearing of personal protective equipment for handlers
- Preparation and submission of standard operating procedure (SOP) to regulatory authority

3.13 ENVIRONMENTAL FATE/DEGRADATION

Antimycin degrades rapidly by hydrolysis in natural waters, and is usually completely broken down within 1–14 days (Finlayson et al. 2002); degradation rates depend on ambient pH and temperature (Morrison 1987). Moreover, as it degrades at high light intensities, antimycin requires dark, as well as cool, storage conditions (Finlayson et al. 2002).

Fintrol, the only available formulation of antimycin in North America, contains some additives (e.g. diethylphthalate) that are of concern to the USEPA and are listed for removal from all pesticides (Finlayson et al. 2002). Although some research was conducted on using mass spectrophotometric and high performance liquid chromatographic techniques to identify antimycin and its metabolites at low concentrations in natural waters, there are currently no validated methods readily available for this purpose and this hindered the reregistration of antimycin in the USA (Finlayson et al. 2002). However, since antimycin has been used successfully for over 30 years with very little evidence of negative environmental or human health effects, the USEPA approved reregistration in 2007 (USEPA 2007).

3.14 TRIGGER VALUE IN NEW ZEALAND

No available data.

3.15 ADVANTAGES

- Rapidly biodegraded.
- Can be detoxified using potassium permanganate.
- Fishes cannot detect the compound so they do not evade exposure.
- Short contact times are required (Gresswell 1991).
- Antimycin is more toxic than rotenone and, because of the smaller quantities required, is sometimes preferred for use in remote locations not accessible by vehicles (i.e. foot or helicopter access only). Depending on the fish species, antimycin is up to 10 times more toxic and requires shorter contact times than rotenone (6 h versus 18 h) (Finlayson et al. 2002).
- Its lower toxicity to bottom-dwelling aquatic invertebrates than some fish species (Morrison 1987) could be an advantage in some management situations.
- Existing data do not suggest any human health concerns (Finlayson et al. 2002).

3.16 DISADVANTAGES

- Antimycin supplies have been unreliable in the past (Marking 1992). The current manufacturer (Aquabiotics Corporation) may have overcome these limitations.
- Antimycin is not registered for use in New Zealand.
- There are currently no validated methods for the detection of antimycin and its metabolites at the concentrations required for environmental effects assessment, which hindered the reregistration of antimycin in the USA (Finlayson et al. 2002). Analytical methods are currently being validated by the US Geological Survey (USEPA 2006).
- Antimycin is very toxic to scaled fishes but is much less toxic to scaleless catfishes (Order Siluriformes), including the brown bullhead (*Ameiurus nebulosus*). This is considered an advantage in North America where the catfishes are farmed, but the brown bullhead is a pest species in New Zealand (Champion et al. 2002; Dean 2003).
- Morrison (1987) states that antimycin A is generally less toxic to bottom-dwelling invertebrates than fishes and is also less toxic to channel catfish, which are not present in New Zealand, although introductions for aquaculture were proposed in the 1980s (Glova 1989).
- Antimycin is neutralised relatively quickly in streams with high gradients (80–150 m decrease in elevation), and its effectiveness also decreases with increasing pH (Finlayson et al. 2002).
- Large amounts of leaf litter or clay turbidity will reduce antimycin toxicity (Gilderhus 1982; Finlayson et al. 2002).

3.17 COMMENTS

Now that antimycin is reregistered in the USA, its registration by ERMA and/or ACVM Group in New Zealand may be more likely. Antimycin offers several advantages over rotenone because it is less toxic to invertebrates, and is not detected by fishes; this may make it worthwhile for antimycin to undergo the registration process in New Zealand. On the other hand, antimycin is an antibiotic, so there are concerns about the development of resistant strains of bacteria.

4. Specific treatment—AQUI-S

4.1 COMPOUND

AQUI-S.

4.2 SYNONYMS/FORMULATIONS

- Isoeugenol
- 2-methoxy-4-propenylphenol
- 4-hydroxy-3-methoxy-1-propenylbenzene
- 4-propenylguaiacol.

(Prepared from eugenol, which is itself prepared from clove oil.)

AQUI-S is 50% isoeugenol (540 g isoeugenol/L) plus an excipient (polysorbate)[4] that improves emulsification of the compound with water. The excipient is a biodegradable, food-grade compound (Jan Holland, AQUI-S Ltd, pers. comm. 2003).

4.3 ACTIVE INGREDIENT

Isoeugenol (CAS Number: 97-54-1).

Note: AQUI-S is not the same as clove oil. Clove oil is 80–85% eugenol, with 15–20% impurities, some of which are toxic (Jan Holland, AQUI-S Ltd, pers. comm. 2003). Clove oil is not registered for either general or veterinary use in New Zealand.

4.4 MECHANISM

Detailed information on the physiological mechanisms of isoeugenol narcosis and toxicity are not readily available.

4.5 USES

It is used as a fish anaesthetic. AQUI-S is the only anaesthetic to be registered in New Zealand that has no withholding period, allowing it to be used for the harvesting of fishes and other seafoods for human consumption.

Isoeugenol is also used in the manufacture of vanillin.

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[4] An excipient is an inactive substance used as a carrier for the active ingredients.

4.6 APPLICATION RATES

Application rates and responses are dependent on the species, size and condition of the fishes being treated. For salmon narcosis, an application of 8 mg/L for approximately 25 min is required, depending on the fish's condition (i.e. rested or stressed) and activity level (i.e. active or undisturbed) (AQUI-S NZ Ltd 2003). An application of 15–20 mg/L is required for anaesthesia after 10–15 min of exposure; higher doses (e.g. 30 mg/L) can be used to produce responses after 2–15 min (AQUI-S NZ Ltd 2003).

AQUI-S has a wide margin of safety when used at low concentrations. Therefore, fish can remain in the treatment mixture for long periods of time without mortalities.

4.7 COST

100 mL: NZ$51	1 L: NZ$345	4 L pack: NZ$1380

Plus freight charges. Discounts apply for large volume or multiple purchases.

AQUI-S is promoted as a cost-effective anaesthetic. Typical costs for harvesting farmed salmon are stated to be 3–5 cents/kg of fish (AQUI-S NZ Ltd 2003).

Treatment of the hypothetical 8000-m^3 pond at 26 mg isoeugenol/L to remove pest fishes after approximately 15-min exposure (i.e. to produce rapid narcosis or death) would require approximately 385 L of AQUI-S (540 g isoeugenol/L) and cost about NZ$133 000 (using the cost for 4 L packs—lower costs could probably be negotiated for large orders). The volume of chemical required is much greater than for antimycin treatment.

AQUI-S is priced mainly for use at low concentrations (17 mg/L) in relatively small volumes of water when fishes have been corralled for handling and husbandry purposes.

4.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

AQUI-S was registered in 1994 with the ACVM Database for use as a veterinary compound[5]. It is approved for use subject to conditions[6], with no withholding period prior to food consumption, and can therefore be used for harvesting seafood. A veterinary prescription is required to purchase AQUI-S, and use of the product is at the discretion of a registered veterinarian, in accordance with the prescription, and applicable codes of practice approved under section 28 of the ACVM Act 1997. The application for its registration in the USA is currently being processed (Jan Holland, AQUI-S Ltd, pers. comm. 2007).

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[5] Clove oil has not been registered by the ACVM Group for use in New Zealand on animals that may be consumed by humans (e.g. for harvesting salmon in an aquaculture operation).

[6] See www.nzfsa.govt.nz/acvm/registers-lists/acvm-register/index.htm (viewed 11 December 2007).

4.9 SOURCE

AQUI-S New Zealand Ltd, 6 Aglionby Street, Lower Hutt, New Zealand 5010. Ph: 64 4 587 0389; Fax: 64 4 587 0388.

4.10 TARGET

AQUI-S is used during the harvesting of food fishes (e.g. salmon) and the transport of fishes (e.g. eels), shellfish (e.g. paua, *Haliotis iris*) and lobster.

4.11 NON-TARGET

Fishes, shellfish and crustaceans.

Few studies have been undertaken to assess the effect of isoeugenol or AQUI-S on aquatic plants and invertebrates (HERA 2005). An industry-generated human and environmental risk assessment of isoeugenol for use as a fragrance (e.g. in washing powders, cleaning sprays, dishwashing detergents) reported no data were available for algae or fish (HERA 2005). In a daphnid immobilisation test, the EC_0,[7] EC_{50} and EC_{100} were 3.8, 7.5 and 15 mg/L, respectively, after 48 h of exposure (HERA 2005).

In an unpublished New Zealand study of the toxicity of isoeugenol, the 72-h EC_{50} for a freshwater alga (*Pseudokirchneriella subcapitata*) was 10.4 mg/L, and the NOEC[8] was 4.8 mg/L (Clearwater et al. 2005)[9]. Juvenile rainbow trout (*Oncorhynchus mykiss*) were more sensitive than the algae were (96-h LC_{50} = 5.1 mg/L; NOEC = 4.2 mg/L), but 48-h cladoceran (*Daphnia magna*) immobility was less sensitive (24-h EC_{50} = 17.9 mg/L; NOEC 6.3 mg/L) than either algal growth or fish survival. However, the 21-day chronic *D. magna* reproduction test yielded the most sensitive endpoint (EC_{50} = 1.1 mg/L; NOEC = 0.4 mg/L) (Clearwater et al. 2005).

No information is available (e.g. on the ACQUIRE Ecotox Database, USEPA 2003) on the toxicity of isoeugenol to aquatic plants.

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[7] EC_0 refers to the concentration that affects 0% of individuals exposed to the test conditions or substance.

[8] NOEC refers to the concentration that produced no observed effect.

[9] Although the report generated by NIWA is confidential and not publicly available, the data are used here with permission from AQUI-S NZ Ltd.

4.12 HUMAN HEALTH

AQUI-S has been approved for use in the harvesting of seafood for human consumption with no withholding period, and is considered to have minimal negative effects on human health when used as directed on the label. AQUI-S NZ Ltd reported that both the active ingredient and the excipient are approved substances, classified by the USFDA as 'food additives permitted for direct addition to food for human consumption' (USFDA 2003: 60, 62).

Isoeugenol is a contact allergen, and the International Fragrance Association (IFRA) has recommended that isoeugenol should not be used at a level that exceeds 0.02% in consumer products (White et al. 1999). Gloves and safety glasses should be used when handling the product.

4.13 ENVIRONMENTAL FATE/DEGRADATION

Chemical data indicate that isoeugenol is unlikely to bioaccumulate in aquatic organisms (log K_{ow} = 2.1[10]) (HERA 2005). A 100-mg/L isoeugenol solution (not AQUI-S) achieved 79% biodegradation after 28 days, and was classified as 'readily biodegradable[11] (HERA 2005).

However, AQUI-S is not quite as biodegradable. An unpublished biodegradation study of AQUI-S undertaken by NIWA for AQUI-S NZ Ltd[12] reported that the ratio of biochemical oxygen demand (BOD) to theoretical oxygen demand (ThOD) (expressed as % ThOD) was 58% and 54.2% ThOD in 2 mg/L and 4 mg/L solutions, respectively, after a 10-day degradation window. This means that AQUI-S was marginally below the OECD lower limit (60% ThOD) for 'readily biodegradable' in freshwater (Macaskill 2000). The failure to achieve the readily biodegradable classification was attributed to the stability and antibacterial properties of the surfactant used in the AQUI-S formulation (Macaskill 2000). In seawater, the 2 mg/L and 4 mg/L AQUI-S solutions had 38% ThOD after the 10-day degradation window and could not be categorised as having clear potential for biodegradability (Macaskill 2000). Abiotic transformation of isoeugenol to biodegradable intermediates was suggested as the probable cause for the low biodegradability rating (Macaskill 2000).

The density of isoeugenol (1.08 g/cm^3) (HERA 2005) means that some sedimentation of the compound will probably occur, especially in seawater. Isoeugenol will disperse initially through diffusion, the rate depending on its use. For example, it will disperse more readily when applied to a partially confined volume of water, such as in a salmon sea-cage, that is part of an open system (the surrounding seawater), than when applied to a closed system, such as a lake or other water body. A small proportion of the isoeugenol will partition to sediments, and microbial degradation will occur when isoeugenol is used at

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[10] Log K_{ow} is the log of the octanol–water partition coefficient and is used to estimate the bioaccumulation of a substance.

[11] OECD 301 Guideline.

[12] Although the report is confidential and not publicly available, the data are used here with permission from AQUI-S NZ Ltd.

the concentrations required for fish toxicity (< 30 mg/L). Concentrations greater than 160 mg/L can inhibit microbial growth (AQUI-S NZ Ltd 2003). Hydrolysis, photolysis and volatilisation are unlikely to contribute significantly to the degradation and dispersion of isoeugenol.

4.14 TRIGGER VALUE IN NEW ZEALAND

No information available. A trigger value would need to be established to set criteria if outflow streams or other obvious discharge areas or zones were present at the application site (e.g. mixing zone around sea-cages).

The proposed predicted no effect concentration (PNEC) for freshwater aquatic organisms in Europe is 4.8 µg isoeugenol/L (HERA 2005).

4.15 ADVANTAGES

- AQUI-S can be used to anaesthetise rather than kill aquatic organisms prior to their harvest, facilitating the sorting of desirable and non-desirable species. However, this use is practical and economical on only a small scale.
- It is possible to use harvested fishes for human or animal consumption, potentially solving disposal problems and/or alleviating public health concerns.
- AQUI-S is a registered, purified product (manufactured to food-grade standards) and ecotoxicological research, albeit unpublished[13], has been completed on its environmental effects and fate (Macaskill 2000; Clearwater et al. 2005).
- AQUI-S has the potential to be used to euthanise pest fishes in a humane manner (for example, after they have been collected prior to a liming operation; section 10).

4.16 DISADVANTAGES

- AQUI-S is a more expensive treatment than some of the other options presented.
- Longer contact times and higher concentrations may be required for mortality, compared to anaesthesia (AQUI-S NZ Ltd 2003), which may be difficult to sustain in field treatments.
- AQUI-S may have negative effects on aquatic plants (we were unable to find any additional information on this subject in our review).

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[13] Studies were undertaken by NIWA on behalf of AQUI-S NZ Ltd in 2000 and 2004, but the results are confidential and have not been published by AQUI-S NZ Ltd.

5. Specific treatment—saponins

5.1 COMPOUND

Saponin(s).

5.2 SYNONYMS/FORMULATIONS

- Teaseed cake: a residue after oil has been extracted from the seeds of *Camellia* spp. (Hu & Cao 1997), e.g. *C. sasangua* and *C. semiserrata* (ICAAE 2003). Varies significantly in quality.
- Mahua oilcake: the cake remaining after oil has been extracted from mahua seeds (*Bassia latifolia*) (Kanaujia et al. 1981).
- SWIMTOP: a product developed in Thailand (early 1990s) that is based on an extract from *Maesa ramentacea*, a fast-growing shrub. We have been unable to find current information on this product and suspect that it has not gone into commercial production.
- Sapogenin glycosides.
- Triterpene glycosides: a subgroup of sapogenin glycosides.

5.3 ACTIVE INGREDIENT

Saponins are a diverse group of mainly plant-derived compounds (there are over 2000 known saponins), also known as 'triterpene glycosides'. They are used: as piscicides; in cosmetics, sweeteners, herbs and non-alcoholic beverages; and for their regulatory effects on crops. Saponins are also found in marine animals. Among the saponin-based piscicides, teaseed cake and mahua oilcake are the two most frequently cited piscicides in peer-reviewed scientific literature; therefore, we have focused on what is known about these compounds.

The saponin content of teaseed cake varies, which is probably due to different production processes and species used. Minsalan & Chiu (1986) reported that teaseed cake contains 5.2–7.2% saponin, but ASEAN (1978) reported that it contains 10–15% saponin.

5.4 MECHANISM

Saponins destroy red blood cells (haemolysis) and therefore reduce oxygen uptake and alter haemoglobin concentrations (Homechauduri & Banerjee 1991). Saponins might also damage the gills of aquatic organisms (Chen & Chen 1998). Crustaceans may be less sensitive to saponins than fishes and saponins have been used in shrimp farming to selectively anaesthetise and/or kill invasive fishes in shrimp ponds (Minsalan & Chiu 1986).

An increase in water temperature or a decrease in dissolved oxygen concentration increases the sensitivity of finfish (e.g. Mozambique tilapia (*Oreochromis mossambicus*) and flathead goby (*Glossogobius giurus*)) to teaseed cake (Minsalan & Chiu 1986).

5.5 USES

Saponins are used to control pest fishes; they are especially used in penaeid shrimp farming as they are less toxic to crustaceans than fishes (Minsalan & Chiu 1986; Chiayvareesajja et al. 1997a). Teaseed cake has been used as a selective poison against fishes at a concentration of 15 mg/L (Minsalan & Chiu 1986), and it may also be used as a fertiliser to condition ponds prior to stocking with shrimp (Mathur et al. 1974; ASEAN 1978). Teaseed cake can also be used to stimulate moulting in shrimp (Hu & Cao 1997), and as a piscicide that is less toxic to nitrifying bacteria than other treatments (Sarkhel & Das 2005).

Teaseed cake and mahua oilcake have been used to kill all unwanted species (e.g. eels, mullets, seabasses and tilapia) in aquaculture ponds prior to stocking for shrimp farming in India (Aquaculture Authority 1999). Following their degradation and decrease in toxicity, the piscicides act as organic fertilisers (Shyam et al. 1993; Aquaculture Authority 1999).

5.6 APPLICATION RATES

5.6.1 Saponins

Saponin may be applied at a rate of 0.5 g/m^3 (i.e. 0.5 mg/L) to remove unwanted fishes (ICAAE 2003). Reduced salinity decreases the toxicity of saponins to fishes. ASEAN (1978) reports that a saponin concentration of 1.1 mg/L killed Mozambique tilapia after a 1-h exposure at 35 ppt salinity. At 10 ppt salinity the same concentration took 14.5–16.5 h to kill the fish. In the Pripyat River in Ukraine, a saponin concentration of 2.0 mg/L was responsible for fish mortality (Grib et al. 2006).

5.6.2 Teaseed cake and SWIMTOP

Chiayvareesajja et al. (1997b) tested the effect of SWIMTOP and teaseed cake (at a concentration of 25 mg/L) on five fish species: *Clarias* sp., common carp, *Gambusia* sp., Nile tilapia (*Oreochromis niloticus*) and Thai silver barb (*Puntius gonionotus*). Over 24 h the lowest mortality occurred in *Clarias* sp. (SWIMTOP: 20% mortality; teaseed cake: 28% mortality), and the highest mortality occurred in Thai silver barb (SWIMTOP: 97% mortality; teaseed cake: 65% mortality).

Chiayvareesajja et al. (1997a) tested teaseed cake and four other species of native Thai plants (*M. ramentacea, Diospyros diepenhorstii, Sapindus emarginatus* and *Pittosporum ferrugineum*) as toxicants against the cladoceran *Moina* sp., the fishes Nile tilapia and climbing perch (*Anabas testudineus*), the shrimp *Penaeus merguiensis*, and the snail *Cerithidea cingulata*, determining the 24-h LC$_{50}$ of each plant for each test species. All of the plant extracts were more toxic to fishes than to the shrimp. The extract from *Diospyros diepenhorstii* was the least effective for all five test organisms, while *M. ramentacea* and *S. emarginatus* provided the most effective plant extracts against *Moina* sp., Nile tilapia and climbing perch. All plant extracts were more effective against Nile tilapia than climbing perch. For the five test species, *Masea ramentacea* showed the highest toxicity to Nile perch (24-h LC_{50} = 15–30 mg/L), but had only half the toxicity of teaseed cake (24-h LC_{50} = 6–15 mg/L). Improvement of the toxicity of *M. ramentacea* is feasible, and both *Pittosporum ferrugineum* and *S. emarginatus* could potentially be used against snail pests (Chiayvareesajja et al. 1997a). The results were considered useful for developing botanical pesticides to selectively kill aquatic organisms.

The published application rates for teaseed cake show some variability between authors, which may be due to the variable saponin concentrations of the products used in their studies. Teaseed cake contains 10–15% saponins according to ASEAN (1978), or 5–7% saponins according to Minsalan & Chiu (1986).

Minsalan & Chiu (1986) applied teaseed cake at concentrations of 10 and 25 mg/L to remove fishes (Mozambique tilapia and flathead goby) from shrimp ponds prior to seeding the ponds. The shrimp species *Metapenaeus ensis* and *Penaeus monodon* both survived concentrations of up to 20 mg/L, but the finfish were eliminated by an application of 15 mg/L.

Teaseed cake may be applied at 0.15–0.20 kg/m^3 (i.e. 200 mg/L) when water is 10–15 cm deep to remove unwanted or 'wild' fishes (ICAAE 2003). The Taiwan Fu Kung Industrial Co., Ltd recommend 150–200 kg/10 000 m^2 for shrimp farms to eradicate pest fishes, and 1500 kg/10 000 m^2 for mussel farms to remove pest fishes and crustaceans[14].

An application of 25 mg/L of teaseed cake resulted in 28–65% mortality after 24 h in a study of the toxicity of teaseed cake on five freshwater fishes in ponds (Chiayvareesajja et al. 1997b).

5.6.3 Mahua oilcake

An application of 0.20–0.25 kg/m^3 (or 250 mg/L) 2 weeks prior to stocking will remove unwanted or 'wild' fishes and the effects will last for 2–8 days depending on the dose used (ICAAE 2003). An application of 100–150 mg/L is recommended for removal of all unwanted organisms from shrimp production ponds in India prior to restocking (Aquaculture Authority 1999). At least 10 days must be allowed for toxicity to be eliminated before restocking (Aquaculture Authority 1999).

5.7 COST

5.7.1 Teaseed cake

The minimum order supplied by Taiwan Fu Kung Industrial Co. Ltd is 20 tonnes in one 1 × 20-foot container at a cost of US$10,000 (plus charges for freight and delivery to Auckland). This price is equivalent to NZ$14,286 (US$1 = NZ$0.70).

Treatment of the hypothetical 8000-m^3 pond at an application rate of 25 mg/L (0.025 kg/m^3) would require 200 kg of teaseed cake, costing NZ$143.

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[14] Application rates were in m^2, and no typical depths were given.

5.7.2 Mahua oilcake

No reliable distribution or price information for mahua oilcake was available.

At an application rate of 0.25 kg/m^3, the hypothetical 8000-m^3 pond would require 2000 kg for piscicidal treatment.

5.7.3 SWIMTOP

No price or distribution information for SWIMTOP was available; it is likely that this product has not gone into commercial production owing to teaseed cake being cheaper to produce.

Application rates are equivalent to 0.015 kg/m^3. Therefore, the hypothetical 8000-m^3 pond would require 120 kg for piscicidal treatment.

5.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

Tea seedcake, SWIMTOP, mahua oilcake and saponins are not registered on the ACVM Database for use in New Zealand.

If the costs of teaseed cake, mahua oilcake and SWIMTOP prohibit their use or if these substances cannot be registered for use in New Zealand, other sources of saponins could be sought and it is highly likely that a plant species already present in New Zealand will be a suitable.

The costs of development and commercial production may not result in a less expensive product than that already available from Asia (see Source below). However, importation of a non-sterilised plant product into New Zealand would present significant biosecurity issues. If the product was fumigated, the effect of the treatment's toxicity to aquatic organisms would have to be considered and perhaps taken into account when determining dosage. Heat treatment might be an option, but it could alter (i.e. reduce) the efficacy of the product.

5.9 SOURCE

5.9.1 Teaseed cake

Teaseed cake is supplied by Taiwan Fu Kung Industrial Co. Ltd.

Contact: Mr S.C. Hsiao, 18 Tong Kuan Street, San Min Dist., Kaohsiung 807, Taiwan. Email: fukung@giga.net.tw; Fax: 886 7 312 6142.

Teaseed cake is also available from Yichun City Linkar Imp. And Exp. Co., Ltd (China) (minimum order 20 tonnes), although no price was available.

Contact: No. 15 Yongfu Road, Majiayuan Market, Around-City Road (East), Yichun, Jiangxi, China 336000.

5.9.2 SWIMTOP

There is no information available on the current commercial status of SWIMTOP; it is likely that it has not gone into commercial production.

Further information can be obtained from:

- www.idrc.ca/en/ev-27176-201-1-DO_TOPIC.html[15]
- Dr Pichaet Wiriyachitra, Research Centre for Natural Products, Faculty of Pharmacy, Chiang Mai University, Chiang Mai 50002, Thailand. Ph: 66 53 217 288; Fax: 66 53 271 360; Email: arunee@chiangmai.ac.th

5.10 TARGET

Targeted organisms have been eels, mullet, sea bass and tilapia, which invade shrimp ponds in Thailand.

5.11 NON-TARGET

Shrimp.

5.12 HUMAN HEALTH

Although practically non-toxic to humans upon oral ingestion, saponins become a powerful haemolytic agent when injected into the blood stream, dissolving red blood cells even at very low concentrations (Budavari et al. 1989).

5.13 ENVIRONMENTAL FATE/DEGRADATION

We were unable to find any scientific publications relating to the environmental fate and degradation of saponins. Teaseed cake, mahua oilcake and SWIMTOP are described in the aquaculture literature as degrading quickly ‘leaving no toxic residues’ (ASEAN 1978; IDRC 1998; Aquaculture Authority 1999). Teaseed cake and mahua oilcake toxicity lasts 2–10 days, depending on dosages (ASEAN 1978; Aquaculture Authority 1999). After application, a minimum period of 10 days should be allowed for the products to degrade and for toxicity to decrease before stocking of the ponds (Aquaculture Authority 1999).

Carp fry can be safely stocked into ponds treated with mahua oilcake after a suitable delay (several days) (Kanaujia et al. 1981; Shyam et al. 1993).

Exposure to 12 h of sunlight reduces the toxicity of teaseed cake to Mozambique tilapia (Minsalan & Chiu 1986).

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[15] Viewed 30 November 2007.

5.14 TRIGGER VALUE IN NEW ZEALAND

No information available.

5.15 ADVANTAGES

- Reported to degrade to non-toxic compounds within 10 days (ASEAN 1978; IDRC 1998; Aquaculture Authority 1999), although no scientific studies were available to confirm this statement.

5.16 DISADVANTAGES

- These piscicidal compounds are prepared from dried and crushed leaves and stems of plants, and may have variable concentrations of the active ingredients. For example, the saponin concentration in teaseed cake can range from 10% to 15% (ASEAN 1978). The variability may be due to factors such as growing conditions of the plants, extraction process and efficiency, and storage time and conditions of the final product.
- Because there are over 2500 triterpene glycosides, it may be difficult to get specific, reliable information on these compounds.
- The simultaneous fertilising effect of these preparations (Aquaculture Authority 1999) may promote undesirable algal growth in some waterways.
- Excessive use of saponins may cause long-term sublethal effects to crustacean immune systems (Yeh et al. 2006).
- Importing a relatively unprocessed plant-derived product into New Zealand would raise some concerns about biosecurity.

5.17 COMMENTS

All saponins foam strongly when shaken with water (Budavari et al. 1989). Teaseed cake should be stored in dry conditions to avoid the development of mould. It can be heated prior to use to remove moisture and for sterilisation.

The potential of plants already growing in New Zealand as sources of saponins merits investigation.

6. Specific treatment—niclosamide

6.1 COMPOUND

- Niclosamide (parent compound)
- Clonitralid (ethanolamine salt of niclosamide).

6.2 SYNONYMS/FORMULATIONS

Bayluscid®; Bayluscide®; Bayer 73®; Bayer 2353®; Bayer 25 648®; Cestocid®; Clonitralid (Germany); Dichlosale®; Fenasal®; HL 2447®; Iomesan®; Iomezan®; Lintex®; Manosil®; Nasemo®; Niclosamid® (Germany); Phenasal®; Tredemine®; Sulqui®; Vermitid®; Vermitin®; Yomesan®.

Common formulations include: an emulsifiable concentrate at 250 g active ingredient/L; a wettable powder at 700 g a.i./L; a 5% aqueous formulation (50 g a.i./L); and a 3.2% granular formulation (32 g a.i./kg).

6.3 ACTIVE INGREDIENT

- Niclosamide (CAS Number: 50-65-7) (Jobin 1979) = 2',5-dichloro-4'-nitro-salicylanilide
- Ethanolamine salt (CAS Number: 1420-04-8 (II)) = Clonitralid
- Piperazine salt (CAS Number: 34892-17-6 (III)), or niclosamide monohydrate (CAS Number: 7336-56-2 (IV)).

6.4 MECHANISM

The mode of action of niclosamide is not completely understood; however, it is thought to uncouple oxidative phosphorylation (Nettles et al. 2001). *In vitro* studies show that niclosamide inhibits rat liver mitochondrial synthesis of ATP (WHO 2003). Bayluscide® inhibits succinate oxidation and causes oxaloacetate accumulation (Ishak et al. 1972).

Water quality alters the toxicity of Bayluscide®. For example, high temperature, low pH (down to pH 7), low hardness and low salinity increase the toxicity of the compound to snails (Tchounwou et al. 1992). At pHs less than 7, however, the solubility of niclosamide decreases (Nettles et al. 2001).

A WHO data sheet (2003) states that:

> 'Niclosamide is a relatively selective, non-cumulative chlorinated aromatic amide pesticide; principally used against aquatic snails but also as an antiparasitic drug in human and veterinary medicine. It is of very low toxicity to mammals (WHO Hazard Class III), can be toxic to aquatic vertebrates (e.g. fishes and amphibians) and crustaceans. Niclosamide is non-persistent in the aquatic environment, has a slight effect on aquatic plants and zooplankton but is not generally phytotoxic at field concentrations.' (WHO 2003)

6.5 USES

Delayed-release and/or pelleted formulations of Bayluscide® are available and have been used in the USA to selectively reduce populations of bottom-associated fish species such as the round goby (*Neogobius melanostomus*). Avoidance response tests indicated that the round goby was unable to detect the compound (Schreier et al. 2001). Also, research on minimum effective contact times indicated that exposure to Bayluscide® for a few minutes is lethal to the round goby, even if the fishes are removed to freshwater immediately afterwards (Schreier et al. 2001).

Niclosamide is sometimes used as a lampricide (Dawson et al. 1998; Nettles et al. 2001; WHO 2003). However, doses of Bayluscide® used to kill sea lampreys can also kill rainbow trout under certain water quality conditions (Nettles et al. 2001). Niclosamide has been used with TFM (a lampricide) to supplement this product and increase its efficacy as a lampricide. It is used in a granular formulation to create high concentrations of niclosamide near the sediment, and thereby target larval sea lampreys, which are burrowing life forms.

Worldwide, however, niclosamide is used primarily as a molluscicide (WHO 2003) and is recommended by WHO for control of schistosome-bearing snails' (WHO 2003), because of its high toxicity to aquatic snails (e.g. *Helisoma trivolvis* and *Biomphalaria havanensis*) (Tchounwou et al. 1991).

It is also used as an antihelminthic in humans, livestock and pets (WHO 2003).

6.6 APPLICATION RATES

WHO (2003) recommends that:

> 'For environmental applications against snails 0.6–1.0 mg/L is effective. In humans over the age of eight, two oral doses of 1 g each, one hour apart for five successive days are usually effective against dwarf tapeworm in individuals 6 years old and over, and 500 mg for younger children. In veterinary medicine single doses ranging from 83–500 mg/kg are recommended.' (WHO 2003)

Note that the goals of treatments recommended by WHO are related to eradication of the snail species that serve as intermediate hosts for human disease (schistosomiasis), and may not place as high a value on minimising effects on non-target species as other types of management programmes would.

Niclosamide is 100% lethal to larval sea lamprey (LC_{100} = 0.06–0.15 mg/L, depending on water hardness[16]) and is more toxic to free-swimming sea lamprey (adults) (12-h LC_{50} = 0.0625 mg/L), than burrowed sea lampreys (larvae) (12-h LC_{50} = 0.110 mg/L) (Nettles et al. 2001). The 24-h LC_{50} for teleost fish species (juveniles) ranges from 0.052 to 0.143 mg/L, with salmonids tending to be more susceptible than other species (Nettles et al. 2001). Niclosamide is toxic to all fish species at 0.5 mg/L (48-h exposure) and to zooplankton and aquatic vegetation at higher concentrations (WHO 2003). In general, hard-bodied invertebrates such as insect larvae and crustaceans are much less susceptible to niclosamide (24-h LC_{50} = 0.8– > 50.0 mg/L) than the soft-bodied invertebrates such as molluscs, leeches, and annelid worms (24-h LC_{50} = 0.03–0.4 mg/L) (Nettles et al. 2001).

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[16] Duration of exposure not reported.

6.7 COST

No price information is available. Bayer Corp was contacted, but although it provided an MSDS for Bayluscid® (Clonitralid), it could not provide a price for use in New Zealand.

6.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

Niclosamide is not registered in New Zealand on the ACVM Database (PAN North America 2003), but clonitralid formulations of niclosamide are registered in the USA as a granular lampricide, a wettable powder, a technical grade product and an emulsifiable concentrate.

6.9 SOURCE

US Fish & Wildlife Service and Bayer Corp.

6.10 TARGET

Niclosamide has been used on the aquatic snails *Melanoides turberculatus, Physella hendersoni* and *Planorbella duryi*: LC_{50} = 0.062–0.085 mg/L and LC_{99} = 0.149–0.440 mg/L (Francis-Floyd et al. 1997).

Two other freshwater snail species (*Helisoma trivolvis* and *Biomphalaria havanensis*) have been targeted and the results were 100% mortality after 24 h of exposure to 2 mg/L (Tchounwou et al. 1991).

Growth of the freshwater mussel (*Dreissena polymorpha* Pallas, also known as the 'zebra mussel') in water intakes and pipes in Europe has been treated with niclosamide (Hoestlandt 1972).

The freshwater oligochaete *Dero digitata* was targeted in catfish-rearing ponds in the USA (24-h LC_{50} = 0.24 mg/L) (Mischke & Terhune 2001).

Eradication of snails from ornamental ponds in Florida was achieved by an application rate of 1.1 kg/ha of Bayluscide®. The use of Bayluscide® was approved by the Florida Department of Agriculture for use in ornamental ponds in 1994 (Francis-Floyd et al. 1994).

Freshwater snails in a North Cameroon pond study had 100% mortality for concentrations of 0.5, 1.0 and 1.5 mg/L of Bayluscide® (Greer et al. 1996).

A Bayluscide® concentration of 0.30 mg/L was 100% effective in the control of the freshwater snails *Biomphalaria stramineus* and *Amularia* spp., but did not harm four species of tilapia (Nile tilapia, *Tilapia hornorum*, redbreast tilapia (*T. rendalli*) and the hybrid *T. hornorum* × *T. niloticum)* (Rezende de Melo & Studart Gurgel 1981). Concentrations of 0.45–0.55 mg/L had different effects on the different tilapia species, and 0.75 mg/L was lethal for all of the fish species (Rezende de Melo & Studart Gurgel 1981), which shows that it could possibly be used as a selective toxicant depending on its effect on New Zealand native species.

In India, a laboratory trial of Bayluscide® resulted in 100% mortality of the freshwater snail *Indoplanorbis exustus* at a concentration of 1 mg/L after 6–9 h of exposure (Koshy & Alwar 1974).

The control of sea lampreys was also undertaken in North America using Bayluscide®. A state-approved application rate of 100 lb/acre (0.011 kg/m^2) was used in 1983 and 1985 and was relatively effective when the intended application rates were achieved, with minimal effects on non-target species (Nettles et al. 2001).

6.11 NON-TARGET

Niclosamide is generally toxic to crayfish, frogs, clams and other aquatic organisms at concentrations higher than those used to kill molluscs (Francis-Floyd et al. 1997; Nettles et al. 2001; PAN North America 2003). WHO (2003) reported that niclosamide is toxic to all fish species at 0.5 mg/L (48 h of exposure) and to zooplankton and aquatic vegetation at high concentrations.

Bayluscide® was found to be less toxic to striped bass (*Morone saxatilis*) fingerlings (72 h of exposure, LC_{50} = 1.05 mg/L) than to freshwater snails (Wellborn 1971).

Exposure of a catfish species (*Clarias lazera*) to predicted sublethal concentrations (0.1 and 0.3 mg/L) of Bayluscide® for 6 months caused immunosuppression resulting in subsequent mortalities of the fish (Faisal et al. 1988). However, when Bayluscide® is used as a molluscicide, exposures are very short (hours to days), and adverse effects on fish would not be expected.

Although no avoidance behaviour was observed in ruffe to Bayluscide®-dosed water in an avoidance chamber, the fish did show increased swimming behaviour and surfacing activity with bottom-release formulations (Dawson et al. 1998).

There may be adverse affects on tadpoles (Eastern spadefoot toad, *Scaphiopus holbrooki* and North American bullfrog *Rana catesbeiana*; LC_{50} of 0.198 mg/L), and mosquitofish (*Gambusia holbrooki*; LC_{50} of 0.657 mg/L) at application rates used to eliminate freshwater snails (LC_{50} = 0.062–0.085 mg/L and LC_{99} = 0.149–0.440 mg/L) (Francis-Floyd et al. 1997) At higher concentrations, turtles would be adversely affected: the red-eared slider (*Trachemys scripta*) had an LC_{50} of 4.909 mg/L (Francis-Floyd et al. 1997).

No adverse effects were noted for the non-target crayfishes *Procambarus alleni* and *P. paeninsulanus* (10 mg/L for 24 h) (Francis-Floyd et al. 1997).

The marine unicellular alga *Skeletonema costatum* had an EC_{50} for Bayluscide® of 0.064–0.081 mg/L (Ibrahim 1983). Three freshwater algae (*Scenedesmus dimorphus*, *S. quadricauda* and *Ankistrodesmus falcatus*) showed a similar sensitivity to Bayluscide® as freshwater snails, with 48-h EC_{50} values of 0.270, 0.175 and 0.176 mg/L, respectively (Ibrahim 1987). Staples et al. (1995) found that growth of the marine alga *Chondrus crispus* was sensitive to 24 h exposures of niclosamide at concentrations from 0.1 to 0.5 mg/L.

Niclosamide is relatively non-toxic to birds and bees if applied as recommended (WHO 2003).

6.12 HUMAN HEALTH

Niclosamide leaves a residue of niclosamides in fish flesh (Schreier et al. 2000).

It is relatively non-toxic to humans: niclosamide is used as an oral tablet for the control of tapeworms. Occasional gastrointestinal upset is the only side effect reported (WHO 2003).

Skin irritation is sometimes reported in workers applying niclosamide, but this is thought to be caused by formulation ingredients other than niclosamide (WHO 2003).

6.13 ENVIRONMENTAL FATE/DEGRADATION

After an application of 1.1 kg/ha to a 0.06-ha pond, niclosamide was detected in the water at a concentration of 0.2–0.4 mg/L after 1 h, and 0.2 mg/L after 25 h. In the pond sediment, niclosamide was transiently detected 7 h after treatment, but not 18 h or 25 h after treatment (i.e. < 0.3 mg/L) (Francis-Floyd et al. 1997). In Florida, ornamental fishes were safely stocked in ponds 10–14 days post-treatment for snail eradication (Francis-Floyd et al. 1994). Niclosamide is removed from natural waters by photochemical degradation, biodegradation and binding to sediments (Nettles et al. 2001). Although it is taken up by organisms, bioconcentration factors are low and not considered significant. Niclosamide appears to be rapidly metabolised and depurated (Nettles et al. 2001).

6.14 TRIGGER VALUE IN NEW ZEALAND

Not available.

6.15 ADVANTAGES

- Useful as a molluscicide if any non-native, invasive mollusc species are found in New Zealand.
- Very low toxicity to humans and other mammals.
- Owing to its low toxicity to mammals, it has been investigated for use as an antifoulant in piping used for drinking water supplies.

6.16 DISADVANTAGES

- Not registered in New Zealand.
- May adversely affect lamprey, fishes and algal species in New Zealand at concentrations used to eliminate molluscs.

6.17 COMMENTS

Slow-release and 'bottom-release' formulations are available to target different species, but these may cause avoidance behaviour in some fishes (Dawson et al. 1998).

Slow-release formulations in ethylene-vinylacetate copolymer (EVA) are available for the long-term control of snails (El-Nagar et al. 1991).

7. General treatment—deoxygenation using dry ice

7.1 COMPOUND

Dry ice (frozen CO_2).

7.2 SYNONYMS/FORMULATIONS

None.

7.3 ACTIVE INGREDIENT

Carbon dioxide (CO_2).

7.4 MECHANISM

Dry ice added to water displaces the dissolved oxygen (DO) in the water, thereby decreasing its concentration, which has a negative effect on fishes. The increased CO_2 concentration has a weakly anaesthetic action on fishes. Using dry ice to add CO_2 might be more effective than other approaches (discussed below) because of the rapid and prolific formation of bubbles around the ice, helping to rapidly 'strip' oxygen from the water.

The minimum DO concentration necessary for fish survival depends on the duration of the exposure, the level and constancy of the DO concentration, and other environmental conditions such as water temperature. Not only do different fish species have widely differing tolerances to low DO concentrations, but other more immediate factors will contribute to the effectiveness of dry ice such as the fishes' level of activity during the exposure, their long-term acclimation to adverse conditions and their stress tolerance (Dean 1999). Salmonids are considered to be the most sensitive group of fishes to low DO levels, and water with a DO concentration of 1–3 mg/L will cause mortality or loss of equilibrium in salmonids (Dean 1999). When concentrations decrease to about 3–4 mg/L, fishes start gasping for air at the surface, and some species (e.g. eels) may leave the water entirely (Dean 1999). Other species such as tilapia are notoriously tolerant to low DO concentrations, and will cope by surface-breathing (skimming the air–water interface) and practising other behaviours (Stickney 1993).

We have been unable to find any published scientific studies on the use of CO_2 for the eradication of pest fish. Increasing CO_2 concentrations by either bubbling the pressurised gas directly into water, or by the addition of sodium bicarbonate ($NaHCO_3$) has, however, been used to sedate fishes during transport or to allow handling of large numbers of fishes, with minimal residual toxicity (Brooke et al. 1978; Bowser 2001). It may be possible, therefore, to use this approach to harvest pest fishes as they lose consciousness, although it will probably be difficult to maintain sufficiently high CO_2 concentrations (Bowser 2001), particularly in natural water bodies.

Carbon dioxide gas is soluble in water and, as such, has weakly acid properties. Typically, the gas is bubbled into the water, but it is difficult to control the concentration of carbon dioxide by this method (Bowser 2001). When $NaHCO_3$ is dissolved in water, it slowly releases CO_2 gas. The gas is released more rapidly under conditions of low pH. Exposure to $NaHCO_3$ at a concentration of 142–642 mg/L for 5 min can anaesthetise fish (Brooke et al. 1978; Bowser 2001). In laboratory trials, a combination of pH 6.5 and 642 mg/L $NaHCO_3$ was the most effective treatment for rainbow trout, brook trout and common carp, causing the fish to cease locomotion and slowing opercular rate within 5 min (Brooke et al. 1978).

The addition of dry ice to rapidly deliver a high dose of CO_2 and simultaneously decrease DO concentrations may be a more effective approach to narcotise pest fishes and other aquatic organisms.

7.5 USES

Dry ice is used for gas shielding during welding and carbonation.

7.6 APPLICATION RATES

Dry ice can be applied as granules using a spreader.

The dose rate for this application is not known. For deoxygenation, we estimate that the concentration of CO_2 would need to be at least 2–5 times the concentration of oxygen. For our comparative analysis, we used a factor of five, so for a water body with a DO concentration of 10 mg/L, we estimate that at least 50 mg/L of CO_2 would be required to deoxygenate the pond.

7.7 COST

20 kg of dry ice costs NZ$57.80 (i.e. $2.89/kg) plus GST from BOC Gas. Deoxygenation of the hypothetical 8000-m^3 pond would require about 400 kg of dry ice assuming a starting DO concentration of 10 mg/L. This would cost NZ$1156 plus GST.

7.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

Carbon dioxide is available in New Zealand. It is not registered on the ACVM Database for use in New Zealand as an agricultural product or veterinary medicine. Carbon dioxide is approved by ERMA for use in New Zealand. In the USA, the use of CO_2 is approved only for anaesthetic purposes for cold, cool and warm-water fishes, rather than for euthanasia (Yanong et al. 2007). Carbon dioxide is listed as a Low Regulatory Priority compound by the American FDA (Bowser 2001).

7.9 SOURCE

Dry ice is available from several sources, including BOC Gas.

7.10 TARGET

Short periods (c. 1 day) of deoxygenation combined with increased CO_2 would affect most aquatic organisms, but would probably affect fishes more than invertebrates because narcosis occurs at higher DO concentrations in fish compared to invertebrates. On the other hand, many species of fishes can tolerate relatively long periods of low DO by behavioural adaptations such as surface-breathing or retreating to refuges (e.g. deep pools, backwaters) that are not affected by the treatment. Deoxygenation would have to be combined with activities such as decreasing the water levels, strategic netting and trapping. The effects on plants are not known but are expected to be minimal.

7.11 NON-TARGET

All species of aquatic organisms could be affected if deoxygenation persists. It is not known how long macrophytes would persist in the absence of oxygen. It may be preferable to apply the treatment at night during calm conditions to minimise the input of oxygen by phototrophs.

7.12 HUMAN HEALTH

A major issue is potential asphyxiation for handlers if dry ice is stored in confined spaces, or if applied when there is no wind, as cold CO_2 gas is much heavier than air and could accumulate at the pond surface. Freezing burns could occur during handling of dry ice. Appropriate safety equipment (e.g. insulated gloves and respirators) must be used when handling and applying dry ice to a water body.

7.12.1 MSDS

Material safety data sheets (MSDS) are available for dry ice.

7.13 ENVIRONMENTAL FATE/DEGRADATION

The water body could be re-oxygenated after a predetermined treatment period in order to stimulate rapid recovery to pre-treatment conditions.

7.14 TRIGGER VALUE IN NEW ZEALAND

Not applicable.

7.15 ADVANTAGES

- Low handling toxicity.
- Low cost.
- Efficacy is easily measured (by DO meter).
- Rapid recovery of water body.
- No residual toxicity issues.

7.16 DISADVANTAGES

- Potential effects on non-target species.
- The time required for deoxygenation is not known and trials would need to be undertaken to determine efficacy and operational issues. Despite the advantages of low cost, and low residual toxicity, it may not be practical to use this method to deoxygenate an entire water body for long enough to affect and remove pest species. These methods are mostly likely to be effective on smaller, less complex water bodies (e.g. small artificial farm ponds).
- Poorly known dosing requirements; possibly large losses of CO_2 to the atmosphere during treatment.
- Dry ice will simultaneously decrease the water temperature and CO_2 concentrations. Fishes are more tolerant of hypoxia at lower temperatures; indeed fishes will seek out cooler areas as the DO concentration declines.

7.17 COMMENTS

This approach requires validation of the quantities required. This could easily be undertaken in tank trials. Chemical deoxygenation would result in a more controlled and sustained deoxygenation (see section 8).

8. General treatment—deoxygenation using sodium sulphite

8.1 COMPOUND

Sodium sulphite and other sulphite compounds.

8.2 SYNONYMS/FORMULATIONS

Sodium sulphite (Na_2SO_3).

8.3 ACTIVE INGREDIENT

Sodium sulphite.

8.4 MECHANISM

This approach utilises the oxygen-scavenging ability of sulphite-containing chemicals to remove oxygen from solution. The advantage of this approach over the microbially-mediated approach (section 9) is the greater level of control in dosing and the more rapid recovery of the water from the deoxygenated condition.

A range of sulphite-containing compounds may be used to undertake the deoxygenation. The major limitations would be in the supply of bulk chemicals and the variability in rate of deoxygenation between chemicals. Some chemicals (e.g. sodium sulphite) may require a metal catalyst (cobalt) for rapid reaction.

Reaction: $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

No pH change or by-products are produced.

8.5 USES

Sodium sulphite is used for scavenging oxygen from boiler waters and is used during pulp and paper processing.

8.6 APPLICATION RATES

It could be applied either as granules using a spreader, or as a liquid.

A minimum application rate could be calculated assuming the DO concentration is 10 mg/L. To allow for loss by re-aeration, partial respiration and photosynthetic production by algae and macrophytes during the application, we would assume a 50% addition by these processes and treat the water body as if 15 mg O_2/L were present (this correction factor may need to be refined). Removal of 15 mg/L of DO would require 118 mg/L of sodium sulphite.

The ratio of sodium sulphite and other sulphite compounds required to remove 15 mg O_2/L (which allows for the 50% addition discussed above) is listed in Appendix 1.

8.7 COST

The price for sodium sulphite varies with the weight purchased:

> 1000 kg:	NZ$0.95/kg	500 kg:	NZ$1.50/kg
250 kg:	NZ$2.00/kg	< 250 kg:	NZ$5.00/kg

Sodium sulphite is imported into New Zealand in large quantities for use in the pulp and paper industry and is always available in large quantities.

At an application rate of 118 mg/L to remove oxygen at a DO concentration of 15 mg/L (which includes 50% to account for re-aeration), the hypothetical 8000-m^3 pond would require 944 kg of sodium sulphite. This would cost NZ$950 if the sodium sulphite was purchased at $0.95/kg for 1000 kg.

8.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

Available in New Zealand. Sodium sulphite is not approved by the ACVM Group as an agricultural compound, but it is approved by ERMA.

8.9 SOURCE

Sodium sulphite is available in bulk from Orica Chemicals. Ph: 09 368 2700.

8.10 TARGET

It would be used for aquatic organisms in general. As with deoxygenation using dry ice, fishes would probably be most affected, followed by aquatic invertebrates. It is unlikely that short periods (c. 1 day) of deoxygenation would affect aquatic plants.

Deoxygenation of water using sodium metabisulphite and/or hydrogen sulphide has been used in cooling water systems for the control of zebra mussels (Matthews & McMahon 1995).

Extended periods of anoxia may be required to kill molluscs such as zebra mussels and Asian clams (*Corbicula fluminea*) (12–25 days at > 20°C; Matthews & McMahon 1995). However, the great anoxia tolerance of both these species below 15°C suggests that anoxic treatment is unsuitable for bivalve control at low temperatures.

8.11 NON-TARGET

All species could be affected if deoxygenation persists. It is not known how long macrophytes would persist in the absence of oxygen. It may be best to apply the treatment at night to minimise the input of oxygen by phototrophs.

8.12 HUMAN HEALTH

Avoid skin and eye contact and breathing in the dust. The oral LD_{50} for mice is 820 mg/kg.

8.12.1 MSDS

Material safety data sheet (MSDS) available from Orica Chemicals.

8.13 ENVIRONMENTAL FATE/DEGRADATION

Sodium sulphite undergoes rapid degradation with no residual products.

8.14 TRIGGER VALUE IN NEW ZEALAND

Not applicable.

8.15 ADVANTAGES

- Low handling toxicity.
- Low cost.
- Efficacy is easily measured (by DO meter).
- Rapid recovery of water body.
- No residual toxicity issues.

8.16 DISADVANTAGES

- Potential effects on non-target species.
- The time required for deoxygenation is not known and trials would need to be undertaken to establish efficacy and operational issues. Despite the advantages of low cost, and low residual toxicity, it may not be practical to use this method to deoxygenate an entire water body for long enough to affect and remove pest species. Repeated dosing may be required to achieve long-term hypoxia; alternatively, another deoxygenation chemical (e.g. sugar) with a more gradual and long-term effect could be added. These methods are mostly likely to be effective on smaller, less complex water bodies (e.g. small human-made farm ponds).
- May require a cobalt catalyst at 0.1 mg/L to achieve very rapid deoxygenation—note that neither ANZECC (2000) nor the USEPA (1999b) provide a cobalt guideline. A requirement to use cobalt would probably render the treatment expensive and unacceptable at this concentration. The rates of deoxygenation without cobalt may well be acceptable for this purpose and would need to be established with tank trials with the site water prior to application to the appropriate water body.

8.17 COMMENTS

This approach appears to be attractive because of the ease of use, low toxicity to humans, lack of residual toxicity and low chemical cost.

We are not aware of precedents for the large-scale use of chemical deoxygenation in natural water bodies. However, deoxygenation with sodium metabisulphite and/or hydrogen sulphide has been used for the control of zebra mussel infestations in water intake structures in the Great Lakes (Mathews & McMahon 1995). If a significant biomass of mussels in a cooling water system is killed by such a treatment, the resultant microbial degradation and other processes could lower pH and produce sulphide compounds leading to corrosion of the pipes and other metal structures. This problem can be minimised by strategies such as routine treatment of fouling organisms to prevent the accumulation of biomass.

The rate of deoxygenation using sodium sulphite in a natural water body in the absence of a catalyst remains to be confirmed.

Other approaches to deoxygenation in cooling water systems include the strategic use of hypoxic water from the hypolimnion in stratified water bodies.

9. General treatment—deoxygenation via microbial methods

9.1 COMPOUND

Substrates for microbial growth such as sugar ($C_6H_{12}O_6$), molasses, whole milk or lactose.

9.2 SYNONYMS/FORMULATIONS

Not applicable.

9.3 ACTIVE INGREDIENT

Sugar ($C_6H_{12}O_6$), molasses, whole milk or lactose ($C_{12}H_{22}O_{11}$).

9.4 MECHANISM

This approach utilises the ability of microorganisms to remove oxygen from solution during aerobic respiration.

Bulk sugar oxidation by microorganisms:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

This equation illustrates that to remove 1 part of dissolved oxygen, 0.94 parts of sugar (by weight) are required.

9.5 USES

The compounds used for microbial deoxygenation are also used for confectionary, foodstuffs and animal feed (molasses).

9.6 APPLICATION RATES

Sugar could be applied as granules using a spreader, or premixed and applied as a solution. Molasses would probably require dilution prior to application to facilitate dispersal.

Application as a solution (sugar or molasses) may require physical mixing (e.g. using outboard motor, or the addition of circulating pumps to the water body) to improve distribution throughout a water body.

A minimum application rate could be calculated assuming there is 10 mg/L of DO in the water. To allow for loss by re-aeration, partial respiration and photosynthetic production by algae and macrophytes during the application, we would assume a 100% addition by these processes and treat the water body as if the DO concentration was 20 mg/L (this correction factor may need to be refined). Removal of 20 mg/L of DO would require 18.8 mg/L of sugar.

9.7 COST

Sugar (refined): NZ$1/kg

Molasses: NZ$1/kg, plus GST (excludes freight and drum).

Treatment of the hypothetical 8000-m^3 pond would require 150.4 kg of sugar. This would cost NZ$150 for refined sugar or molasses.

9.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

All these forms of sugar are available in New Zealand. Molasses is approved by the ACVM Group as a bloat remedy, and approved by ERMA for import and manufacture for inclusion in veterinary medicines.

9.9 SOURCE

Sugar: New Zealand Sugar Company.

Molasses: BLM Holdings Ltd. Ph: 06 755 3344,; Fax 06 755 3321; Email: blmholdings@xtra.co.nz

Milk: Wholesalers and dairy companies.

9.10 TARGET

It is used for aquatic organisms in general. As with deoxygenation using dry ice or sodium sulphite, fishes would probably be most affected, followed by aquatic invertebrates. It is unlikely that short periods (c. 1 day) of deoxygenation would affect aquatic plants. However, sugar-containing compounds deoxygenate water more slowly than the chemical deoxygenation methods, and reoxygenation takes longer. The latter will result in an extended period of hypoxia compared with those methods. This could be used to advantage, depending on the target species and the types of environmental impacts that will be acceptable for the water body to be treated.

9.11 NON-TARGET

All species would be affected if deoxygenation persists. It is not known how long macrophytes would persist in the absence of oxygen.

The water body could be reoxygenated after a predetermined treatment period.

9.12 HUMAN HEALTH

No issues.

9.12.1 MSDS

Not required.

9.13 ENVIRONMENTAL FATE/DEGRADATION

A variable rate of loss by oxidation with no toxic by-products.

9.14 TRIGGER VALUE IN NEW ZEALAND

Not applicable.

9.15 ADVANTAGES

- Low handling toxicity.
- Low cost.
- Efficacy is easily measured (by DO meter).
- No residual toxicity issues.

9.16 DISADVANTAGES

- Potential effects on non-target species.
- Prolonged deoxygenation may result in high mortality to plants.
- The rate of deoxygenation may be highly variable, but we estimate that the intended dexoygenation could take 2–4 days. Recovery of oxygen levels may be slow because of ongoing oxidation of the sugars.
- Depending on the application technique and how effectively the compounds were pre-mixed, sugar or molasses might not completely degrade during the initial treatment and remain in the sediment. These compounds could be resuspended after the initial treatment, resulting in a repeat deoxygenation of the water body.

9.17 COMMENTS

This microbial deoxygenation approach may be attractive because of the ease of use, low toxicity to humans and lack of residual toxicity. However, the variable rate of deoxygenation (and therefore the lower level of control), slower onset and the slow recovery may favour more precise chemical deoxygenation for many water bodies.

We are not aware of precedents for large-scale use of microbial deoxygenation. However, the rapid deoxygenation of rivers and resulting fish kills from milk spillage have been documented (e.g. McBride 1982b), and the rate of deoxygenation both of milk and sugar solutions measured (Hickey & Nagels 1985) and predicted for natural waters (McBride 1982a).

10. General treatment—lime

10.1 COMPOUND

Lime.

10.2 SYNONYMS/FORMULATIONS

- Calcium carbonate ($CaCO_3$) = limestone = agricultural limestone
- Calcium oxide (CaO) = quicklime = burnt lime
- Calcium hydroxide ($Ca(OH)_2$) = hydrated lime = slaked lime.

10.3 ACTIVE INGREDIENT

$Ca(OH)_2$ is preferred for pest control operations.

10.4 MECHANISM

Lime addition is used to increase the pH and alkalinity[17] of water or soils to lethal concentrations for the target organisms (Clearwater 2006). The most likely mechanism of toxicity is that extreme changes in water chemistry cause direct physical damage to the gills of most aquatic organisms and disrupt respiration and iono-regulation. Macrophytes will also be physically damaged by extreme alkalinity (Piper et al. 1998).

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[17] The total quantity of titratable bases in water includes bicarbonates, carbonates and hydroxides balanced against the concentration of protons, and is expressed as $CaCO_3$ mg/L (Wurts & Masser 2004).

Lime can be applied to the dried pond bottom or the water surface. When used to eradicate pest aquatic organisms it is added as hydrated lime to water at high applications rates sufficient to increase $pH > 2$ for 4–5 days (Clearwater 2006). More moderate applications of lime are used to manipulate pond water and soil chemistry (i.e. alkalinity, hardness[18] and pH) to enhance aquaculture operations (Boyd & Tucker 1998; Mazik & Parker 2001; Wedemeyer 2001).

10.5 USES

Liming is a non-specific treatment and will kill most aquatic organisms present, therefore this approach to pest eradication is appropriate only in water bodies where it is acceptable to completely disrupt the aquatic ecosystem (e.g. small, enclosed human-made ponds with limited outflow). In addition, the majority of aquatic animals would probably be killed by caustic injury to the gills and other delicate respiratory and dermal surfaces, which is likely to inflict pain. Because no information on the humaneness of lime application could be obtained, it is recommended that a cautious approach is taken and that liming operations be planned to avoid direct eradication of the pest organisms and non-target species. A summary of current knowledge of liming follows.

Lime is used routinely in earthen ponds for aquaculture operations to manipulate the water and soil chemistry and increase productivity (Boyd & Tucker 1998; Mazik & Parker 2001; Wedemeyer 2001; Wurts & Masser 2004). Lime application at low rates causes minor to moderate changes in soil and water chemistry and is known as 'pond conditioning'. For example, liming with limestone is used to increase the pH of acidic soils and enhance organic decomposition. Limestone is less soluble than other forms of lime and therefore changes pond chemistry slowly, with less risk to the aquaculturist. Increased alkalinity will stabilise the pH of pond water, which can vary from pH 6 to pH 10 during the day if the alkalinity is less than 20 mg $CaCO_3$/L (Wurts & Masser 2004). Hardness is also important to aquatic organisms. Calcium and magnesium are essential for: bone and scale formation; osmoregulation; molting of crustaceans; and hardening of newly formed shells (Wurts & Masser 2004).

At high application rates, burnt lime or hydrated lime (which are more soluble than limestone) can be used to 'disinfect' ponds by temporarily increasing soil or water pH and alkalinity to levels sufficient to kill any parasites and disease micro-organisms present (Piper et al. 1998). However, some pathogens, including those that cause human disease, are not be affected by high pH (Mazik & Parker 2001).

Lime can also be used to eradicate aquatic pest species, by application at exceedingly high rates to increase the pH of pond water to lethal levels (Clearwater 2006). In order to be effective against most aquatic species the pH must be increased to pH 12 for at least 24 h, as some species, e.g. marron (*Cherax tenuimanus*) are resistant to exposures of 12 h to water with a high pH (> 9.5). Lime may also be ineffective against organisms that can avoid or limit their

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[18] The total concentration of divalent cations (e.g. Ca^{2+}, Mg^{2+}, Fe^{2+}), expressed as mg $CaCO_3$/L (Wurts & Masser 2004).

exposure (e.g. by burrowing). Macrophytes will probably be killed or damaged by these extreme liming treatments (Piper et al. 1998).

Burnt and hydrated lime are more soluble than limestone and so are preferable when a rapid change in pH and alkalinity is required. Burnt lime is more soluble, but also more caustic than hydrated lime. Therefore, hydrated lime has usually been used in field-scale aquatic operations in order to minimise human health and safety concerns (Clearwater 2006).

The use of lime to eradicate aquatic pests has not been systematically studied, so much remains unknown about the effect of factors such as application rate, the exposure time required to kill pest species, pest species resistance, and recovery rates of treated water bodies (Clearwater 2006). Field data on recent liming operations against aquatic pests in Australia and New Zealand have recently been reviewed for DOC (Clearwater 2006). In summary, liming has been used in eradication attempts (not systematic scientific studies) against gambusia, goldfish (*Carrasius auratus*), grass carp, gudgeon (*Gobio gobio*), koi carp (*C. carpio*), marron, rudd (*Scardinius erythrophthalmus*), tench (*Tinca tinca*), and yabbies (*Cherax destructor*) (Dykzeul & Young 2001; IFS 2003a, b, 2004; David 2003; Barnes 2005). The limited follow-up data indicate that the eradication of pest fishes was generally successful, but that the crustaceans (marron and yabbies) were resistant when pH was < 12. These results led to the recommendation that in order to ensure the effective eradication of all pest organisms the pH should be increased to pH 12 for at least 24 h or for 4–5 days if resistant species are present. Alternatively, to rapidly kill resistant species, the addition of a small quantity of ammonium sulphate once pH was over 10 has been suggested (e.g. Barnes 2005) (see section 11).

The typical procedure for a liming operation is to decrease the water volume to a manageable size (and filtering the extracted water to remove pest organisms including their eggs and larvae), then to remove as many of the remaining aquatic organisms as possible by netting and trapping. These organisms are then sorted into pest species and treated accordingly (e.g. euthanised using approved methods or released), thereby minimising pain and suffering. Lime is then applied (preferably as a pre-mixed slurry) to the remaining water to rapidly increase the pH to 12. This high pH is maintained for 4–5 days, or another compound such as ammonium sulphate is added to rapidly kill any resistant organisms (discussed in detail in section 11). The exposed banks and vegetation can also be treated with lime if necessary.

Limed ponds treated at moderate application rates for aquaculture conditioning or disinfection can be restocked approximately 10 days after treatment or when the pH has decreased to below 9.5 (normal pH = 6–8) (Piper et al. 1998). Pond water productivity (e.g. phyto- and zooplankton levels) will not return to normal until 3–4 weeks after treatment (Piper et al. 1998). Recovery of pre-treatment conditions usually takes longer if the pH has been maintained above 12 for several days. For example, Dykzeul & Young (2001) found that a lime-treated pond had a pH of 9.0 3 weeks after treatment. However, the return to initial pH and alkalinity will be dependent on many factors including the water flow and exchange rates in the treatment area, and local water and soil chemistry (Clearwater 2006). The pH and alkalinity can be measured and used to determine when to restock.

10.6 APPLICATION RATES

Piper et al. (1998) suggest that an application rate equivalent to 0.1–0.3 kg/m^3 is required to raise the pH above 10[19]. Evidence from field work for pest eradication in Australia and New Zealand suggests that rates of 0.6–3.1 kg/m^3 are required to maintain the pH sufficiently high to eradicate pests (i.e. pH > 12 for 4–5 days) (Dykzeul & Young 2001; IFS 2003a, b, 2004; Barnes 2005). One operation used 44.4 kg/m^3 to eradicate koi carp and maintain pH at 11.1 for 0.5 h (David 2003). These application rates are, however, best estimates from the limited field data that have been reported, and the applicators were not necessarily trying to minimise lime quantities or accurately measure water volumes (Clearwater 2006).

Exact application rates will depend on the local soil and water chemistry (specifically, the pH and alkalinity) and the quality of the (usually hydrated) lime (Boyd & Tucker 1998; Piper et al. 1998; Mazik & Parker 2001). For example, a major factor in the efficacy of treatment is the solubility of the lime, which is influenced strongly by particle size (Boyd & Masuda 1994). Smaller particle sizes will dissolve more readily. Boyd & Masuda (1994) developed a grading system to classify the wide range of liming materials available for bulk application on agricultural land by primary compound (e.g. burnt or hydrated lime), neutralising value and particle size. It is also recognised that hydrated lime is unstable in storage and over time will convert to limestone, so, before use, the 'activity' of the lime can be tested by measuring the change in water temperature produced by the addition of a standard quantity of product (ASTM International 2007). A major advantage of using lime is that direct measurement of pH (as a surrogate for alkalinity) during application can be used to monitor the effect on water chemistry and application rates can be adjusted as required.

Only limited follow-up field information was available on the recovery of hardness and alkalinity to pre-treatment concentrations (Clearwater 2006). New Zealand waters are regarded as mostly 'soft' (i.e. less than 50 mg $CaCO_3$/L, Hickey 2000), and the addition of large amounts of lime to a pond to raise pH to over 12, would increase both the alkalinity and hardness to extreme levels. Extremely high alkalinity is likely to be more detrimental to aquatic organisms than extremely high hardness. Reduction of alkalinity to concentrations acceptable for aquatic plants and invertebrates following liming may take some considerable time. The Australasian field data show that pre-treatment conditions were achieved within 24 h in some cases (Dykzeul & Young 2001); in others, pH was still elevated after 3 weeks (Dykzeul & Young 2001) and 3–5 months (IFS 2004) post-treatment, despite the application of acid to assist recovery. Obviously, if the goal of the treatment is recovery of the treated water body to pre-treatment conditions, then the lowest possible application rates should be used. A combination of control measures may sometimes be the most effective approach. For example, Barnes (2005) reported being able to eradicate pest fish species with relative ease by liming, but the high pH-resistant marron had to be treated with ammonium sulphate to ensure 100% mortality.

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[19] Calculated from the recommended application of 1000–2500 lb/acre if 1 m deep.

10.7 COST

Prices vary with the volume purchased and bagging and freighting charges. The following prices for hydrated lime ($Ca(OH)_2$) as a fine powder (c. 95% < 90 μm) were obtained from McDonald's Lime Ltd.

20 kg bags: NZ$275/tonne	Tanker (22 tonnes): NZ$218/tonne.

Plus GST and freighting charges of about NZ$15/tonne in the Waikato region.

Treatment of the hypothetical pond (volume: 8000 m^3), at application rates of 0.6–3.1 kg/m^3 reported for most of the field data from Australia and New Zealand, would require 4800–24 800 kg of hydrated lime at a cost of NZ$1320–6820 (plus GST and freight).

10.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

Available in New Zealand as a fertiliser. Burnt lime (CaO) is approved by the ACVM Group as a bloat remedy. Hydrated lime is approved by the ACVM Group as a parenteral nutrient and electrolyte supplement. ERMA registration of lime as a fertiliser already exists.

10.9 SOURCE

Source:	McDonald's Lime Ltd.
Contact:	Duncan Clark or Peter Rolles. Ph: 07 873 8024; Freephone: 0800 245 463; Fax: 07 873 7829; Mobile: 021 841 998.

Other suppliers are also available (listed under 'Lime Works' in the New Zealand Yellow Pages).

10.10 TARGET

All aquatic organisms, especially pest fishes and disease organisms.

10.11 NON-TARGET

All aquatic organisms.

10.12 HUMAN HEALTH

Burnt lime and hydrated lime are much more soluble in water than limestone and therefore are used in liming operations when pond sterilisation and pest eradication are the goals (Boyd & Tucker 1998). However, burnt lime is a strongly caustic agent which may cause severe irritation of the skin and mucous membranes (Budavari et al. 1989); therefore, from a human health perspective most operators will prefer to work with hydrated lime (rather than burnt lime). Hydrated lime can also irritate the skin and mucous membranes but is significantly less caustic and reactive than burnt lime. In addition, burnt lime is more unstable than hydrated lime and will absorb CO_2 and water from air; therefore, it must be stored in dry, air-tight conditions. Personal protective equipment (i.e. gloves, goggles, overalls, boots) is required when handling burnt or hydrated lime.

10.13 ENVIRONMENTAL FATE/DEGRADATION

The major advantage of using lime for pest eradication is that even though high application rates of lime will have a large impact on a water body, lime is not considered a persistent toxin (especially by the general public), even though its effects could last for months. Lime is a naturally occurring compound, consisting of some of the most abundant elements on earth, in compounds that are highly abundant (Boyd & Tucker 1998).

Liming will produce a rapid increase in water alkalinity and pH. The addition of lime to water has the potential to cause an initial short-term increase in water temperature up to 70°C (Hassibi 1999). We have been unable to locate any evidence that water temperatures have significantly increased during liming of outdoor ponds.

Water alkalinity, hardness and pH will return to initial conditions over time, the period of time depending on many factors including: water flow and exchange rates through the water body, and local water and soil chemistry (Boyd & Tucker 1998; Piper et al. 1998). Using the lowest possible application rate, and strategies such as addition of ammonium sulphate, will help to ensure rapid recovery to pre-treatment conditions.

Liming of eutrophic waters can cause precipitation of phosphorus; this precipitate will remain on the sediment after treatment (Wang et al. 2005).

In the context of the application of lime to a water body, degradation is perhaps best defined as the return of local soil and water chemical parameters (especially pH and alkalinity) to pre-application conditions. Changes in soil chemistry are likely to persist for months or years after a lime application, especially if the liming compounds were not fully mixed at application, thereby causing the settlement of lime particles on the sediment.

10.14 TRIGGER VALUE IN NEW ZEALAND

There are no relevant ANZECC trigger values for lime or related compounds. However, the original pH (6–9) may need to be restored by dilution of the treated water, or the addition of acid following treatment.

10.15 ADVANTAGES

- If used strategically, the addition of lime will have relatively short-term effects on the water body.
- Direct measurement of pH can be used to determine the efficacy of lime application.
- The breakdown products of the treatment are naturally occurring minerals.
- Lime application could be combined with the addition of ammonium sulphate at high pH to increase the toxicity of both treatments, and decrease the duration of exposure required for the effective eradication of pest species.

10.16 DISADVANTAGES

- Lime will act as a general toxicant and will kill or damage all aquatic life, including macrophytes.
- As liming is likely to inflict pain, most fishes and large invertebrates should be removed from the water body prior to lime treatment so that the pest species can be sorted out and euthanised. This cautious approach is recommended to make the treatment as humane as possible.
- Algal blooms may occur following treatment.
- The high pH will also be dangerous to other organisms (e.g. birds) until it is reduced; access to the treated water body will have to be prevented.
- Decaying organic matter resulting from lime treatment could cause anoxic conditions in the treated water body.
- As pH and alkalinity may not decrease to acceptable levels for an extended post-treatment period, it may be necessary to dilute the water or neutralise pH and alkalinity.

10.17 COMMENTS

Liming of a water body to eliminate aquatic pest species is a non-specific treatment option best suited for artificial environments such as human-made ponds and aquaculture operations in earthen ponds. A lime treatment would cause significant disruption to a natural water body, including the requirement to decrease water volumes pre-treatment and to net and trap most fishes or large invertebrates. This negative effects of this disruption would have to be weighed against the benefits of the elimination of a pest species.

11. General treatment—ammonia

11.1 COMPOUNDS

- Ammonium sulphate plus hydrated lime
- Urea and bleaching powder.

11.2 SYNONYMS/FORMULATIONS

- Ammonium sulphate ($(NH_4)_2SO_4$) plus hydrated lime ($Ca(OH)_2$)
- Urea ($(NH_2)_2CO$) + bleaching powder ($Ca(ClO)_2$).

11.3 ACTIVE INGREDIENT

Un-ionised ammonia (NH_3) and the ammonium ion (NH_4^+).

11.4 MECHANISM

Ammonia is highly toxic to aquatic organisms as it interferes with osmoregulation at the gills and disrupts the blood chemistry (ANZECC 2000; Eddy 2005). Ammonia is the main end product of protein metabolism and a major excretory product of fishes (Piper et al. 1998). A combined lime treatment and ammonium sulphate application takes advantage of the fact that ammonia is much more toxic to aquatic organisms at higher pH values.

Ammonia is a non-persistent and non-cumulative toxicant to aquatic biota (ANZECC 2000). The complex chemistry and speciation of ammonia in aqueous solutions (un-ionised ammonia NH_3 and the ammonium ion NH_4^+) has been described in many publications (e.g. USEPA 1999c; ANZECC 2000; Eddy 2005). The proportions of NH_3 and NH_4^+ are related to pH, temperature, salinity and the permeability of biological membranes to the NH_3 and NH_4^+ forms (Eddy 2005). The proportion of the more toxic form (NH_3) increases rapidly as the pH and temperature increase (Piper et al. 1998). For freshwater, at pH 8.0 and 20°C, the proportion of NH_3 is 3.82%. At pH 9 and 10, the proportions increase to 28.4% and 79.9%, respectively (Emerson et al.1975). In freshwater, NH_3 has been identified as the major cause of toxicity, owing to the fact that biological membranes are more permeable to it than to the NH_4^+ ion (Eddy 2005). However, the membranes of marine organisms may be more permeable to the NH_4^+ ion, in which case NH_4^+ may contribute significantly to toxicity (Eddy 2005). Proportionally, though, pH and interspecific differences have a much greater affect on ammonia toxicity than salinity.

For estimating toxicity, the joint toxicity of both forms of ammonia should be considered (Eddy 2005), and both the USEPA (1999c) and ANZECC (2000) guidelines are for the total ammonia concentration at a particular pH, taking into account the relative toxicity of both forms of ammonia.

The use of urea and bleaching powder is probably targeted at achieving a long-acting biocide resulting from the reactive combination of the two ingredients. Few reliable references were available to provide a basis for this approach. Urea is a slow-release source of ammonia, so it is combined with bleaching powder (a source of hypochlorite ions), which we suggest produces chloramines which are highly toxic to aquatic organisms.

Ammonia and hypochlorite ions react to form a number of products, depending on the temperature, their concentrations, and how they are mixed. The main reaction is chlorination of ammonia, first giving chloramine (NH_2Cl), then $NHCl_2$ and finally nitrogen trichloride (NCl_3). These materials are very irritating to eyes and lungs and are toxic to aquatic organisms above certain concentrations (ANZECC 2000).

$NH_3 + OCl^- \rightarrow OH^- + NH_2Cl$

$NH_2Cl + OCl^- \rightarrow OH^- + NHCl_2$

$NHCl_2 + OCl^- \rightarrow OH^- + NCl_{3.}$

The formation of high levels of chloramines is undesirable owing to persistence, tainting and bioaccumulation concerns. Therefore, we would not recommend the compounds as piscicides in natural ecosystems.

11.5 USES

Anhydrous ammonia is used in refrigeration systems and chemical manufacturing, but is extremely hazardous and, therefore, would be unsuitable for direct application as a piscicide in field situations.

Ammonium sulphate is also used as a fertiliser to add nitrogen to deficient soils. It is relatively safe to handle.

Urea is used as fertiliser to add nitrogen to deficient soils.

Bleaching powder is used in water treatment (aquaculture, swimming pool chlorination) and as a sanitiser, cleaning agent and sterilising agent.

11.6 APPLICATION RATES

The toxicity of ammonia to aquatic organisms may be estimated from the USEPA AQUIRE Ecotox database (USEPA 2003). In its derivation of the Criterion Maximum Concentration (CMC) for ammonia, the USEPA (1999c) ranked 34 genus mean acute values (derived from acute LC_{50} or EC_{50} values) for ammonia ranging from 12.1 to 388.8 mg/L total ammonia-N, at pH 8.0. Generally, fishes are more sensitive to it than invertebrates (ANZECC 2000). The least sensitive fish (*Cottus bairdi*, mottled sculpin) had an acute value of 51.73 mg NH_4-N/L. The most sensitive fish species (*Prosopium williamsoni*, mountain whitefish) had an acute value of 12.11 mg NH_4-N/L. Based on these values, we estimated that the total ammonia concentration in a water body required for 100% eradication of pest fishes, using lime to increase the pH to 10, could be as low as 25 mg NH_4-N/L. However, the USEPA (1999c) acute ammonia values are for juvenile fishes, and include only five species. Accordingly, we have used a multiplication factor of 4–10 times to account for large fishes likely to be present in a water body requiring pest fish treatment, and recommend that for use as a piscicide on a range of freshwater pest fish species in New Zealand, the required total ammonia concentration should be 100–200 mg NH_4-N/L at pH 10. Lower concentrations may be used if more sensitive species are the target.

The application of liquid ammonia would cause rapid death of aquatic organisms, but liquid ammonia is dangerous to handle, so this approach is not recommended for field situations. Sinha (1985) reported that anhydrous ammonia applied at 15–20 mg/L was an effective piscicide, and also acts as a fertiliser.

Ammonium sulphate is reasonably easy to handle and is available in crystal (sugar-like) or granular forms. Once applied to water, ammonium sulphate lowers the pH, effectively reducing the un-ionised ammonia component. An application of 10–20 kg/ha at 1–4 week intervals (equivalent to 0.001–0.002 kg/m^3 for a 1-m deep pond) is recommended for pond fertilisation (Boyd & Massaut 1999). Therefore, for use as a piscicide, ammonium sulphate is most effectively used in conjunction with a lime treatment, to first increase the pH with lime, thereby increasing the toxicity of the ammonia (Kungvankij et al. 1986). As an estimate, Piper et al. (1998) recommended that 0.1–0.3 kg/m^3 of lime would be sufficient to raise the pH to 10. We estimate that the required total ammonia concentration in the water body should be 100–200 mg NH_4-N/L at pH 10. If the ammonium sulphate has a nitrogen content of 0.205 kg N/kg fertiliser, 0.49–0.98 kg/m^3 would be required.

The use of urea and bleaching powder is probably targeted at producing a long-acting biocide through the use of the reactive combination of the two ingredients. Few reliable references were available to provide a basis for this approach.

Urea gives a delayed response as ammonia is produced only upon degradation. In addition, large, impractical quantities would be required to produce sufficiently toxic concentrations of ammonia. However, when urea is combined with bleaching powder, urea is an effective piscicide at relatively low application rates (Ram et al. 1988; Mohanty et al. 1993). In aquaculture ponds, applying urea 24–48 h before applying bleaching powder to achieve 3–5 mg total N/L and 5 mg chlorine/L was found to be the most effective treatment for 100% fish kill within 1 h of application (Ram et al. 1988; Mohanty et al. 1993). Crustacean and mollusc death also occurred within 1–24 h (Ram et al. 1988, Mohanty et al. 1993). In a field trial, minnows and weed fishes were the most sensitive, and carps and predators the least sensitive (Ram et al. 1988). The ponds recovered sufficiently to start being restocked approximately 10 days post-treatment. Based on urea with a nitrogen content of 0.46 kg N/kg fertiliser, an application rate of at least 0.007–0.011 kg/m^3 would be required to achieve 3–5 mg N/L. Based on a bleaching powder with an available chlorine content of 35%, an application rate of 0.014 kg powder/m^3 would be required to achieve 5 mg chlorine/L.

11.7 COST

Ammonium sulphate $(NH_4)_2SO_4$

NZ$385/tonne plus GST, from Ravensdown Ltd (based on an N:P:K:S rating of 20.5:0:0:24, yielding 0.205 kg N/kg fertiliser).

Hydrated lime ($Ca(OH)_2$) from McDonald's Lime Ltd:

20 kg bags: NZ$275/tonne	Tanker (22 tonnes): NZ$218/tonne.

Plus GST and freighting charges of about NZ$15/tonne in the Waikato region.

Treatment of the hypothetical 8000-m^3 pond at 100–200 mg NH_4-N/L and pH 10, would require an application rate of 0.49–0.98 kg/m^3 and therefore would require 3920–7840 kg of ammonium sulphate at a cost of NZ$1509–3018.

According to Piper et al. (1988), 0.1–0.3 kg/m^3 of hydrated lime ($Ca(OH)_2$) would be required to raise the pH to 10. Therefore, approximately 800–2400 kg would be required for a 8000-m^3 pond, at a total cost of $220–660. However, these application rates could vary significantly from our estimates because the quantity of lime required to increase the pH to 10 is highly site specific.

Urea $(NH_2)_2CO$

NZ$595/tonne plus GST, from Ravensdown Ltd (based on an N:P:K:S rating of 46:0:0:0, yielding 0.46 kg N/kg fertiliser).

Using bleaching powder ($Ca(OCl)_2$) with 35% available chlorine for a 5 mg/L available chlorine dose in the theoretical 8000-m^3 pond would require 114 kg of bleaching powder, at a cost of NZ$803. The application rate would be 0.014 kg powder/m^3.

Treatment of the 8000-m^3 pond at 5 mg NH_4-N/L would be an application rate of 0.011 kg/m^3 and therefore would require 87 kg of urea at a cost of NZ$52.

The total cost (excluding GST) for this treatment would be NZ$855.

11.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

Both ammonium sulphate and urea are available in New Zealand and are used as fertilisers. Lime is also used in agriculture and widely available. Bleaching powder is used in industry and agriculture for cleaning and sterilisation. None of these substances are approved by the ACVM Group. Registration and classification by ERMA already exists, subject to conditions.

11.9 SOURCE

Ammonium sulphate and urea can be obtained from fertiliser distributors (e.g. Ravensdown or Ballance):

www.ravensdown.co.nz www.ballance.co.nz[20]

Hydrated lime can be obtained from local or regional suppliers (e.g. McDonald's Lime Ltd).

Contact: Duncan Clark or Peter Rolles. Ph: 07 873 8024; Freephone: 0800 245 463; Fax: 07 873 7829; Mobile: 021 841 998. www.onlime.co.nz[21]

Bleaching powder can be obtained from industrial chemical suppliers (e.g. Select Chemicals Ltd, Hamilton. Ph: 849 7185).

11.10 TARGET

The lime plus ammonium sulphate and urea plus bleaching powder treatments are based on the toxicity of ammonia and chloramines, which are both general toxicants. Ammonia and/or chloramines would be toxic to all species at the recommended application rates. Although some invertebrates are slightly less sensitive to ammonia than fishes are (USEPA 1999c), our recommended highest application rate would result in the death of most fishes and invertebrates.

11.11 NON-TARGET

Ammonia is highly toxic to aquatic organisms, and the effect on non-target species would depend on the application rate. If the ammonia concentration were sufficiently high, all species would be adversely affected. Of particular concern in New Zealand would be the potential for adverse effects on native fishes in the treatment area. The sensitivity of native fishes to ammonia is similar to, or lower than the sensitivity of the species used to develop the USEPA (1999c) guidelines (Richardson 1997; Hickey 2000). Adjusted to pH 10, the 96-h LC_{50} values of native fish species would be 0.94–2.94 mg NH_4-N/L, and the 24-h LC_{50} values would be 1.15–> 6.1 mg NH_4-N/L. The fish acute values (adjusted to pH 10) used for the USEPA (1999c) guidelines for ammonia are 2.44–6.7 mg NH_4-N/L. These data indicate that the use of ammonia as a piscicide for pest fishes species at the recommended application rates would also result in the death of any native fishes present in the treatment area. The numbers of native fishes affected could be minimised by reducing the volume of the treatment area, and netting and sorting native species from pest fishes before application of the chemicals.

The pH should be neutralised and water quality guideline compliance assessed prior to any discharge from a treated water body.

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[20] Viewed 10 December 2007.

[21] Viewed 10 December 2007.

11.12 HUMAN HEALTH

Liquid ammonia is an extremely hazardous substance and therefore the use of anhydrous ammonia or ammonia solutions is inadvisable in field situations.

Ammonium sulphate is relatively safe to handle, but irritates respiratory surfaces and skin with prolonged exposure. Basic personal protective equipment (e.g. gloves) should be used when applying large quantities of it to water. Equipment for respiratory protection should be considered if it is to be applied as a fine powder.

Hydrated lime is caustic to human skin and respiratory surfaces. To minimise risk, use personal protective equipment (e.g. gloves, goggles, boots, overalls), including approved respiratory equipment if it is to be applied as a fine powder in large quantities.

Urea is safe for humans to handle; however, the application of bleaching powder (hypochlorite solution) will require safety precautions (e.g. use of gloves, goggles, approved respiratory equipment, overalls and boots). Bleaching powder is an oxidiser, and will severely irritate skin, eyes and respiratory surfaces. It must be stored in a dry environment separate from strong reducing agents, strong acids and organic material (Mallinckrodt Baker Inc. 2006).

Because, as mentioned, bleaching powder is a strong oxidising agent (and a base), mixing it with ammonia solutions or urea may produce toxic and/or explosive ammonia trichloride vapours, so the two compounds must be stored separately.

11.13 ENVIRONMENTAL FATE/DEGRADATION

The addition of nitrogen (as ammonia) might cause post-treatment eutrophication of the water body. The degradation of ammonia will probably be slow, although it might be possible to reduce the post-treatment ammonia toxicity by adding acid to the treatment pond. Lime treatment is accepted has having minimal negative effects in the long-term, with non-toxic degradation products.

Chlorine compounds can react with organic compounds in natural waters to form persistent chlorinated organic by-products (e.g. trihalomethanes, haloacetic acids and chlorite) in low concentrations (USEPA 1999d). These compounds are of concern because, for example, they have been shown to be carcinogenic to laboratory animals. Therefore, the long-term discharge of chlorine-treated wastewaters is not encouraged by the USEPA, and dechlorination is required to minimise the effects on human health and aquatic organisms (USEPA 1999d, 2006a). On this basis, we would not recommend the use of urea and bleaching powder for use in natural ecosystems where alternatives can be found.

11.14 TRIGGER VALUE IN NEW ZEALAND

0.3–2.3 mg NH_4-N/L (total ammonia) at pH 8 (ANZECC 2000).

11.15 ADVANTAGES

- Ammonia is completely biodegradable.
- Ammonia is effective against all aquatic organisms, particularly if used in conjunction with lime to increase the pH, or with bleaching powder to produce chloramines.
- Water quality may return to pre-treatment conditions relatively quickly.
- Some species of invertebrates are less sensitive to ammonia than fishes are; therefore, ammonia could possibly be used to selectively remove pest fish species.

11.16 DISADVANTAGES

- New Zealand native fish species have a similar or greater sensitivity to ammonia compared to pest fishes.
- Eutrophication via nitrogen addition may occur post-treatment.
- Small quantities of potentially toxic and persistent chlorinated organic residuals could be produced; this may cause public concern.

11.17 COMMENTS

The potential for eutrophication effects and for New Zealand native fishes to be like exotic fishes in terms of their sensitivity to ammonia make it a less favourable option. Trials using water from the treatment site to establish the application rates and determine the efficacy of the combinations of urea plus bleaching powder or ammonium sulphate plus lime would be advisable before large-scale implementation.

12. General treatment—chlorine

12.1 COMPOUNDS

- Chlorine gas (Cl_2)
- Calcium hypochlorite ($Ca(OCl)_2$)
- Sodium hypochlorite (NaOCl).

12.2 SYNONYMS/FORMULATIONS

- SoftChlor (NaOCl: 125–165 g Cl/L, depending on the age of the solution, and formulation; solutions of different strengths are available).
- Bleaching powder ($CaCl_2O_2$: 25–40% available chlorine).

12.3 ACTIVE INGREDIENT

Chlorine (CAS 7782-50-5).

12.4 MECHANISM

Chlorine is a non-specific poison and will kill most aquatic organisms (Westers 2001). It is a basic industrial chemical used for manufacturing chlorinated and inorganic chemicals. In elemental form, it is gaseous (Cl_2), and very soluble in water (ANZECC 2000). Once dissolved in water, chlorine is rapidly converted to hypochlorous acid (HOCl), hypochlorite ions (OCl^-) and hydrochloric acid (HCl) (ANZECC 2000). The relative proportions of each in equilibrium are determined by the pH, temperature and ionic strength of the solution. At pH 2–7, HOCl is the dominant form. At pH 7.4 and 20°C, there are equal proportions of HOCl and OCl^- (ANZECC 2000).

If ammonia and other nitrogenous substances are present when chlorine is introduced, chloramines form, which constitute ‘combined chlorine’. These compounds are more persistent than free chlorine. The sum of free chlorine and combined chlorine is called ‘total residual chlorine’ (ANZECC 2000). Free chlorine and the chlorine compounds oxidise organic and inorganic matter and are toxic to fishes and all other forms of aquatic life (Westers 2001). Chlorine is a powerful disinfectant that is used in aquaculture to kill any pathogens in culture ponds and tanks (Piper et al. 1998).

12.5 USES

Chlorine is used to treat wastewater and potable water, in aquaculture, to chlorinate swimming pools and as a sanitiser, cleaning agent and sterilising agent.

12.6 APPLICATION RATES

An application of 5–10 mg/L for 1–24 h is sufficient to kill harmful bacteria and all other organisms (Piper et al. 1998); the exact amount depends on the target species and the local water chemistry, particularly the amount of organic matter present.

Chlorine used at a concentration of 5 mg/L will kill most fish species after as little as 1 h of exposure (Westers 2001). Chlorine deteriorates rapidly, and usually loses its toxicity after 1 day at this concentration (Westers 2001).

12.7 COST

12.7.1 Softchlor

Can be purchased in 20-L lots (about 0.16 kg available Cl/L), costing NZ$1.60/L.

Treatment of the hypothetical 8000-m^3 pond at an application rate of 10 mg/L would require 500 L of Softchlor at a cost of NZ$800.

12.7.2 Bleaching powder

Available as 40-kg drums (70% $Ca(OCl)_2$[22], usually equivalent to 25–40% available chlorine), costing NZ$7.03/kg.

Treatment of the hypothetical 8000-m^3 pond at an application rate of 10 mg/L would require 228.4 kg of bleaching powder[23] at a cost of NZ$1606.

12.8 REGISTERED/AVAILABLE IN NEW ZEALAND?

Various forms of chlorine are available in New Zealand. Chlorine is not approved by the ACVM Group as an agricultural compound. Chlorine, calcium hypochlorite and sodium hypochlorite are registered and approved by ERMA, subject to conditions.

12.9 SOURCE

Chlorine is manufactured at pulp and paper plants in New Zealand (e.g. Carter Holt Harvey).

SoftChlor and bleaching powder can be obtained from industrial chemical suppliers (e.g. Select Chemicals Ltd, Hamilton. Ph: 07 849 7185).

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[22] Calcium hypochlorite content varies, depending on manufacturer. Check label for exact content and adjust application rates accordingly.

[23] Based on 70% calcium hypochlorite and 35% available chlorine.

12.10 TARGET

All aquatic organisms.

12.11 NON-TARGET

All aquatic organisms.

12.12 HUMAN HEALTH

Chlorine gas is extremely toxic, and its use is not appropriate for field applications.

Sodium hypochlorite (NaOCl) and calcium hypochlorite ($Ca(OCl)_2$) are oxidisers that promote combustion and that decompose in the presence of heat, water or contamination, with the release of corrosive chlorine gas. Solutions are corrosive to the skin, eyes and upper respiratory tract (Haz-Map n.d.). All chlorine compounds are hazardous to handle. However, the risks can be effectively managed by the use of protective equipment and clothing, and implementation of safety procedures. Short-term exposure to high doses of chlorine and chlorine compounds may be fatal. Long-term exposure to sub-lethal concentrations of fumes and solutions may result in dermatitis, skin lesions and damage to respiratory passages (US National Library of Medicine n.d.).

12.13 ENVIRONMENTAL FATE/DEGRADATION

Chlorine and chlorine compounds are used as disinfectants for treating all kinds of wastewaters (USEPA 1999a, d). Residual chlorine is very toxic to aquatic life; therefore, dechlorination is often required prior to the discharge of treated water to receiving waters (USEPA 1999d). In addition, chlorine compounds can react with organic compounds in natural waters to form persistent chlorinated organic by-products (e.g. trihalomethanes, haloacetic acids and chlorite) in low concentrations (USEPA 1999a). These compounds are of concern because, for example, they have been shown to be carcinogenic to laboratory animals. Therefore, the long-term discharge of chlorine-treated wastewaters is discouraged by the USEPA, and dechlorination is required to minimise the effects on human health and aquatic organisms (USEPA 1999d, 2006a). However, the one-off use of chlorine as a piscicide would be unlikely to produce significant long-term environmental effects. Dechlorination by treatment with sodium sulphite[24] may be advisable if the treatment area is part of a public water supply system or is ecologically sensitive, and if it would also facilitate recovery of the natural community (USEPA 1999d).

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[24] Sulphur dioxide, sodium bisulphite, and sodium metabisulphite are the commonly used dechlorination compounds in the USA (USEPA 1999d).

12.14 TRIGGER VALUE IN NEW ZEALAND

In freshwater, 0.4–13 µg Cl_2/L, for slightly to moderately disturbed systems, depending on the level of protection (ANZECC 2000).

12.15 ADVANTAGES

- Easily neutralised with sodium sulphite.
- Will rapidly kill all pest aquatic organisms.
- Easily detected and measured with portable kits (e.g. those used in swimming pool treatments).

12.16 DISADVANTAGES

- High doses are sometimes required to overcome the chlorine demand of organically enriched waters.
- Potentially toxic and persistent chlorinated organic residuals are produced in small amounts; this may cause public concern.
- Skilled handlers are required.
- It is a general toxicant, with no specificity.

13. Discussion

The treatment options presented fall into two broad categories: specific compounds that offer some species selectivity and general treatments intended to kill all freshwater life in an area. The properties of these potential piscicides and rotenone, the treatment currently used by DOC, are summarised in Appendix 2.

Each of the specific treatments has costs and benefits. A major disadvantage is that only AQUI-S is currently registered and available in New Zealand for aquatic use as a piscicide or molluscicide. This report is intended to provide DOC with information to determine whether a long-term freshwater pest control strategy should include efforts to register products such as antimycin. ERMA registration of new compounds is largely based on whether these products have been successfully registered in North America. For example, as antimycin was successfully re-registered in the USA in 2007, registration in New Zealand might now be feasible and cost-effective.

Plant-derived saponins have been widely used in non-intensive aquaculture operations throughout Asia and Africa and are attractive for the control of aquatic pests because of their low toxicity to mammals (compared to aquatic organisms). If DOC is unsuccessful in registering and importing a saponin-based product from overseas (e.g. teaseed cake), it is highly likely that a native New Zealand plant species could be identified as a suitable source of saponins. There may already be some Maori knowledge of plants with piscicidal properties.

The general treatments tend to be less costly, and we have focused on methods that will not cause any long-term toxic degradation products. In situations where there is a negative public perception of rotenone, chemical treatments such as dry ice, sodium sulphite or liming may be preferred. Nor have we fully analysed the long-term effects of these treatments in situations where aquatic plants would be negatively affected and the nutrient balance of a water body disrupted by the addition of a nutrient such as nitrogen. Limnologists would need to be consulted to determine the likelihood of such effects, and the potential disturbance to freshwater systems would need to be weighed against the value of eradicating pest species on a case-by-case basis. There are management options available to mitigate the short-term effects of complete eradication. For example, a ‘seed’ population of desirable zooplankton could be removed prior to treatment; it could then be returned to the system post-treatment to help reduce any ensuing phytoplankton blooms.

Two major factors that will determine the potential success of these treatments are how well the treatment area is known and the application method used. The American Fisheries Society has produced a handbook for rotenone use that discusses piscicide application issues in detail (Finlayson et al. 2000). It is recommended that ‘streamside’ bioassays are conducted to assess the effect of piscicide toxicity on local water quality conditions, and that dyes such as fluorescein (if compatible with the piscicide) are used to track toxin dispersal (Gresswell 1991).

In addition, some of the treatments involve the use of expensive and/or potentially harmful chemicals. Appropriate protective clothing and equipment must be worn during applications. We also recommend that, depending on the chemical and the management goals, the following additional precautions be considered for inclusion in an operational plan to minimise the potential for adverse effects and accidental exposure (adapted from USEPA 2007):

- Reduce volume to be treated by draining ponds before application
- Remove as many fishes as possible by netting before application, sort pest fishes from non-target species, euthanise pest fishes and relocate non-target species
- Prohibit fish harvesting from treated areas (duration dependent on treatment)
- Prevent access of birds, stock and pets to the treated area while a hazard exists
- Close drinking water intakes, until chemical levels return to acceptable levels
- Prohibit public access to the treated area during and after application (duration dependent on treatment)
- Deactivate outflows and/or neutralise active ingredients (e.g. using potassium permanganate, activated charcoal)
- Require training of and wearing of personal protective equipment by chemical handlers
- Prepare and submit a standard operating procedure (SOP) to appropriate regulatory authorities

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Appendix 1

THE RATIO OF VARIOUS SULPHITE COMPOUNDS REQUIRED TO REMOVE ONE PART OF OXYGEN

The oxygen added through re-aeration and photosynthetic production during sulphite treatment was accounted for by adding 50% to the actual oxygen concentration of the water prior to treatment. For example if the DO concentration was 10 mg O_2/L, we assumed 15 mg O_2/L. So 118 mg Na_2SO_3/L (15 mg O_2/L × 7.9) would be required.

CHEMICAL	PARTS SULPHITE COMPOUND ADDED = PARTS OF OXYGEN REMOVED
Sodium sulphite (Na_2SO_3)	7.9
Sodium metabisulphite ($Na_2S_2O_5$)	5.9
Sodium bisulphite ($NaHSO_3$)	6.5
Ammonium bisulphite (NH_4HSO_3)	6.2

Appendix 2

ANALYSIS OF THE PISCICIDE TREATMENTS OUTLINED IN THIS REPORT AND ROTENONE

Rotenone is the treatment currently used by DOC. The information in this summary table is based on our preliminary review of the scientific literature and ecotoxicology databases detailed in this report. A more detailed ecotoxicological analysis is recommended prior to actual testing of any of these products. N/A = criterion not applicable to the compound concerned. NR = method not recommended.

COMPOUND	REGISTERED IN USA?	AVAILABLE IN NZ?	ACVM REGISTERED IN NZ?	CAN IT BE USED IN NZ AT PRESENT?	COST OF PRODUCT REQUIRED TO TREAT HYPOTHETICAL POND (8000 m^3)	SPECIFICITY (RELATIVE TOXICITY TO DIFFERENT ORGANISMS INDICATED)	HUMAN HEALTH CONCERNS WHEN USED AS DIRECTED	ENVIRONMENTAL EFFECTS	APPLICATION METHOD	RANK FOR USE IN SMALL PONDS (< 1 ha, < 5 m DEEP)	RANK FOR USE IN SMALL LAKES (> 1 ha AND/OR > 5 m DEEP)	RANK FOR USE IN LARGE LAKES (> 5 ha AND/OR > 5 m DEEP; NOT EASILY TREATABLE)	RANK FOR USE IN STREAMS OR RIVERS	RANK AS A PISCICIDE
Piscicides and molluscicides														
Antimycin	Yes	No	No	No	US$2024	Scaled fish > invertebrates > catfish >> plants	None known; some some research has been conducted	Minimal	Sub-surface spray; drip stations; baits possible	High	High	Medium	High	High
AQUI-S[a]	Pending	Yes	Yes	Yes	NZ$133,000	Aquatic organisms >> aquatic plants?	None known; approved for use in food	Minimal; approved for use in NZ and USA	Liquid sub-surface spray; drip stations	High	Medium (cost)	Low (cost)	Medium (cost)	Medium (primarily used as an anaesthetic)
Saponins (Teaseed cake, Mahua oil)	No	No	No	No	NZ$143[b] (teaseed cake)	Fish >> crustaceans >> plants	None known; not necessarily researched	None known; not necessarily researched	Solid product: spreaders or by hand	High	Medium	Low (volume)	Low	High
Niclosamide	Yes	No	No	No	No cost info.	Snails = flukes = nematodies > fish, amphibians, crustaceans > aquatic plants	Minimal toxicity to mammals; used as an oral drug against tapeworms (cestodes, trematodes, nematodes)	Minimal; does not bioaccumulate	Liquid sub-surface spray; drip stations	High	High	Medium	High	Low (molluscicide)
Rotenone (powdered)	Yes	Yes	Yes	Yes	NZ$5061[c]	Fish > invertebrates >> mammals >>> plants	Minimal toxicity to mammals when used as directed	Minimal: can be 'detoxified' if rapid degradation required	Spray as slurry from hoses or helicopter	High	High	Medium	High	High

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[a] Aqui-S is not the same as clove oil. Clove oil is 80–85% eugenol with 15–20% impurities, some of which are toxic (Jan Holland, AQUI-S Ltd, pers. comm. 2003).

[b] Based on an exchange rate of US$1 = NZ$0.7.

[c] Based on a 2007 indicative price from Garrick Distributors Ltd (www.garrick.co.nz; viewed 11 December 2007) of $421.75/25 kg, cube root powder, 8.1% rotenone content; apply at 3 mg/L.

COMPOUND	REGISTERED IN USA?	AVAILABLE IN NZ?	ACVM REGISTERED IN NZ?	CAN IT BE USED IN NZ AT PRESENT?	COST OF PRODUCT REQUIRED TO TREAT HYPOTHETICAL POND (8000 m^3)	SPECIFICITY (RELATIVE TOXICITY TO DIFFERENT ORGANISMS INDICATED)	HUMAN HEALTH CONCERNS WHEN USED AS DIRECTED	ENVIRONMENTAL EFFECTS	APPLICATION METHOD	RANK FOR USE IN SMALL PONDS (< 1 ha, < 5 m DEEP)	RANK FOR USE IN SMALL LAKES (> 1 ha AND/OR > 5 m DEEP)	RANK FOR USE IN LARGE LAKES (> 5 ha AND/OR > 5m DEEP; NOT EASILY TREATABLE)	RANK FOR USE IN STREAMS OR RIVERS	RANK AS A PISCICIDE
General toxicants														
Deoxygenation														
Dry ice	N/A	Yes	No	Yes	NZ$1156	Aquatic organisms >> plants	Minimal	Minimal	Spreaders	Medium	Low	Low	NR	Medium
Sodium sulphate	N/A	Yes	No	Yes	NZ$950	Aquatic organisms > plants	Minimal	Minimal	Spreaders; sub-surface spray	Medium	Medium	Low	Low	Medium
Microbial	N/A	Yes	Yes	Yes	NZ$150	Aquatic organisms > plants	None	Minimal	Spreaders	Medium	Medium	Low	NR	Medium
Lime	N/A	Yes	Yes	Yes	NZ$1320 to $6820	Damages aquatic vegetations as well as aquatic animals	Minimal; protective clothing required during application	Slow return to normal pH; possible algal blooms after application unless managed	Spreaders	Low	Low	Low	Low	Low
Ammonium sulphate (110 mg/L) + Lime	N/A	Yes	No	Yes	NZ$1729 to $3678	Similarly toxic to native NZ fishes as non-natives	Minimal; protective clothing required during application	Eutrophication possible post-treatment	Spreaders; sub-surface drip station to rivers	Medium	Medium	Low	Medium	Medium
Urea + Bleach	N/A	Yes	No	Yes	NZ$855	As above	Minimal; protective clothing required during application	Urea + bleach not recommended because of formation of chloramines	Spreader + spray application	Low	NR	NR	NR	Low
Softchlor, Bleach powder	N/A	Yes	No	Yes	NZ$800 (Softchlor) NZ$1606 (Bleach powder)	General; would kill all aquatic life; more toxic to fish than plants or invertebrates	Minimal; protective clothing required during application	Low concentrations of persistent chlorinated-organics may be produced	Liquid sub-surface spray; drip stations to rivers	Low	Low	Low	Low	Low

How can we kill aquatic pests in New Zealand?

At least 21 species of exotic fish and several species of snail have become established in freshwater systems in New Zealand, some of which pose a significant threat to freshwater biodiversity. One option for minimising their impacts is eradication through the use of chemicals. Rotenone is the main chemical used to control fish internationally, but its use has been very limited in New Zealand to date. This review outlines the advantages and disadvantages of various treatment methods other than rotenone for controlling pest fish and snails in freshwater systems.

Clearwater, S.J.; Hickey, C.W.; Martin, M.L. 2008: Overview of potential piscicides and molluscicides for controlling aquatic pest species in New Zealand. *Science for Conservation 283.* 74 p.

New Zealand Government