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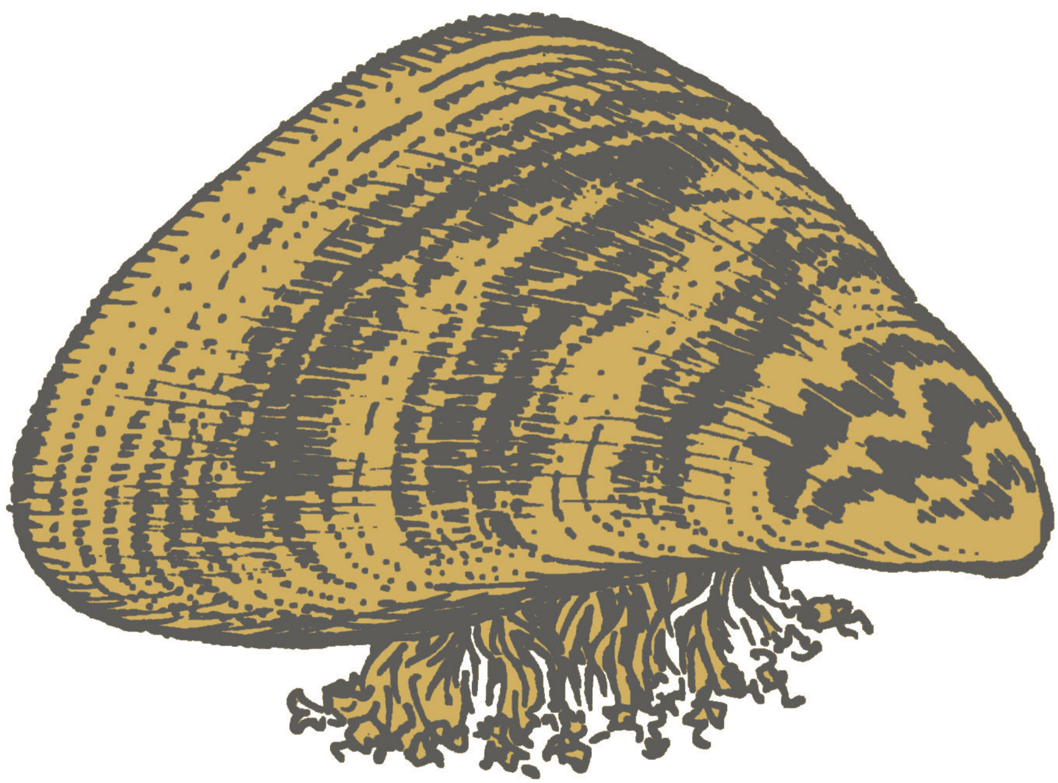
Zebra Mussel Research Program

Zebra Mussel Chemical Control Guide

Susan L. Sprecher and Kurt D. Getsinger

January 2000



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Preface

The work reported herein was conducted as part of the Zebra Mussel Research Program (ZMRP) under Work Unit 33156, “Aquatic Molluscicide Use Guide.” The ZMRP is sponsored by Headquarters, U.S. Army Corps of Engineers (HQUSACE), and is assigned to the U.S. Army Engineer Research and Development Center (ERDC) under the purview of the Environmental Laboratory (EL), Vicksburg, MS. The HQUSACE Technical Monitors for ZMRP are Joe Wilson, Pete Juhle, and Cheryl Smith.

The purpose of this report is to provide guidance to Corps District and Project personnel on the selection and use of registered chemicals available for control of zebra mussels. To assist in the selection process, the various types of compounds that were registered as molluscicides at the time that this report was written are summarized with information on use strategies and application rates.

The Principal Investigator for this study was Dr. Kurt D. Getsinger, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), EL, under the general supervision of Dr. Robert H. Kennedy, Acting Chief, EPEB; Dr. Richard E. Price, Chief, EPED; and Dr. John W. Keeley, Acting Director, EL. Dr. Edwin A. Theriot, EL, was Program Manager of ZMRP. This report was written by Drs. Susan L. Sprecher and Getsinger, EPED. Technical reviews of this report were provided by Dr. H. E. Tatem and Mr. R. M. Stewart, EPED.

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1 Introduction

Background

Control and prevention of macrofouling caused by the freshwater zebra mussel, *Dreissena polymorpha* (Pallas), have been major concerns of managers of all types of water delivery systems since shortly after the arrival of this nuisance species in North America in 1985 (Hebert, Muncaster, and Mackie 1989). The types of operating systems and system components that can be expected to undergo zebra mussel infestations and fouling include those associated with the management and control of inland waterways; potable water treatment; agriculture; industry; and power generation (McMahon, Ussery, and Clarke 1994; Claudi and Mackie 1994).

The threat to lock structures, navigation dams, reservoir control structures, vessel locks, stream level gauging systems, pumping stations, drainage structures, and other structures present in navigable waterways is of particular interest to the U.S. Army Corps of Engineers. The Corps also owns and operates 75 hydroelectric power plants in the United States, all of whose components (intake structures, cooling water, transducers, gauging stations, project irrigation, fire prevention lines, etc.) have been identified as being susceptible to zebra mussel fouling (McMahon and Tsou 1990; Neilson 1992)[1]. Generally, facilities that can be expected to be affected include hydropower dams, nonpower dams, navigation locks, fossil-fueled and nuclear-fueled generating plants, certain types of recreation sites (boat ramps, beaches), and miscellaneous other sites (Tippit, Cathey, and Swor 1993).

In North America, as in Europe, chemical applications to water have been the most commonly used method of zebra mussel treatment and control for internal and closed systems (Claudi and Mackie 1994). Numerous organic and inorganic chemicals are toxic to zebra mussels and can provide versatile, easy to implement, and cost-effective ways to deal with established infestations and to prevent new ones from occurring. Chemicals are expected to be a major control method and to be used as part of integrated control programs in the future. While these treatments can be designed to protect whole systems, their major drawback is the requirement for safe discharge in compliance with environmental regulations.

[1]In 1997 it was estimated that commercial power plants in the Great Lakes region spend $350,000 per year to clear away zebra mussel infestations from these types of areas (Jeffrey Reuter, US CoChair of the Council of Great Lakes Research Managers (CGLRM), address to CGLRM, 1 and 2 November 1997).

Since the arrival of the zebra mussel, a number of chemicals with previously known or newly discovered molluscicidal properties have been proposed for deployment against this highly invasive organism. This report describes basic guidelines for the use of those compounds that are currently registered with the United States Environmental Protection Agency (USEPA) for zebra mussel control, and includes a summary of the important registration process.

Chemical Control of the Zebra Mussel

Mussel life cycle and behavior influence the strategies and tactics of chemical control, as well as choice of molluscicidal compound. Zebra mussels cannot survive in saline conditions but are well adapted to water temperatures (12 ºC to 32 ºC (55 ºF to 90 ºF)), pH range ($6.5 to >8), and turbidity levels that can be found in the Great Lakes and many U.S. riverine environments (Claudi and Mackie 1994; Figure 1). Spawning occurs in spring when water temperatures rise above 12 ºC and can continue into October. Females release up to 30,000 planktonic (free-swimming) larvae, called veligers, which move with water currents and grow up to 1.3 cm (0.5 in.) in the first half year. These settle in colonies and attach to firm surfaces by means of secreted strands called byssal threads. Densities can reach 500,000 per square meter (46,500 or more per square foot), and individual life spans are 3 to 5 years. Zebra mussels are filter feeders, opening their shells to allow ingestion of particulates. When their sensitive chemoreceptors alert them to certain toxins in the environment, they have the ability to maintain shell closure for up to 2 weeks and thereby remain immune to certain biocide contact. Not all molluscicides evoke this response, however.

The application of chemical molluscicides in the field is limited by several considerations. Firstly, a method must be judged by how well it removes or kills the various life stages of the zebra mussel. Secondly, any chemical control method used must not be harmful to natural fisheries and aquatic ecosystems and must also be eventually compatible with possible potable water use. Thus, flow-through systems may require a different suite of chemicals than is possible in static or closed systems where there is no release to the environment. Since chemical control is most suitable for application to problems in closed systems and internal piping, it is much less effective in treatment of external surfaces where it may be impossible to maintain required treatment concentrations and contact times of the compound. Thus, current chemical options are not available for treating and reducing densities of zebra mussels in source waters, such as lakes, rivers, and streams. In these areas nonchemical methods are more suitable. Finally, use of the material must be cost-effective.

Chemicals identified for zebra mussel control have been derived mainly from water treatment compounds and antifouling biocides and biodispersants. Chlorine has been used for nearly a hundred years in drinking water disinfection, where its properties and behavior in effluent are well known, and it has been the primary chemical for zebra mussel control in Europe. In contrast, molluscicidal properties have been associated only recently with endothall, a compound used for several decades as an aquatic herbicide. Investigation of toxicity to both the target and nontarget organisms in the aquatic environment is the first step in the ongoing

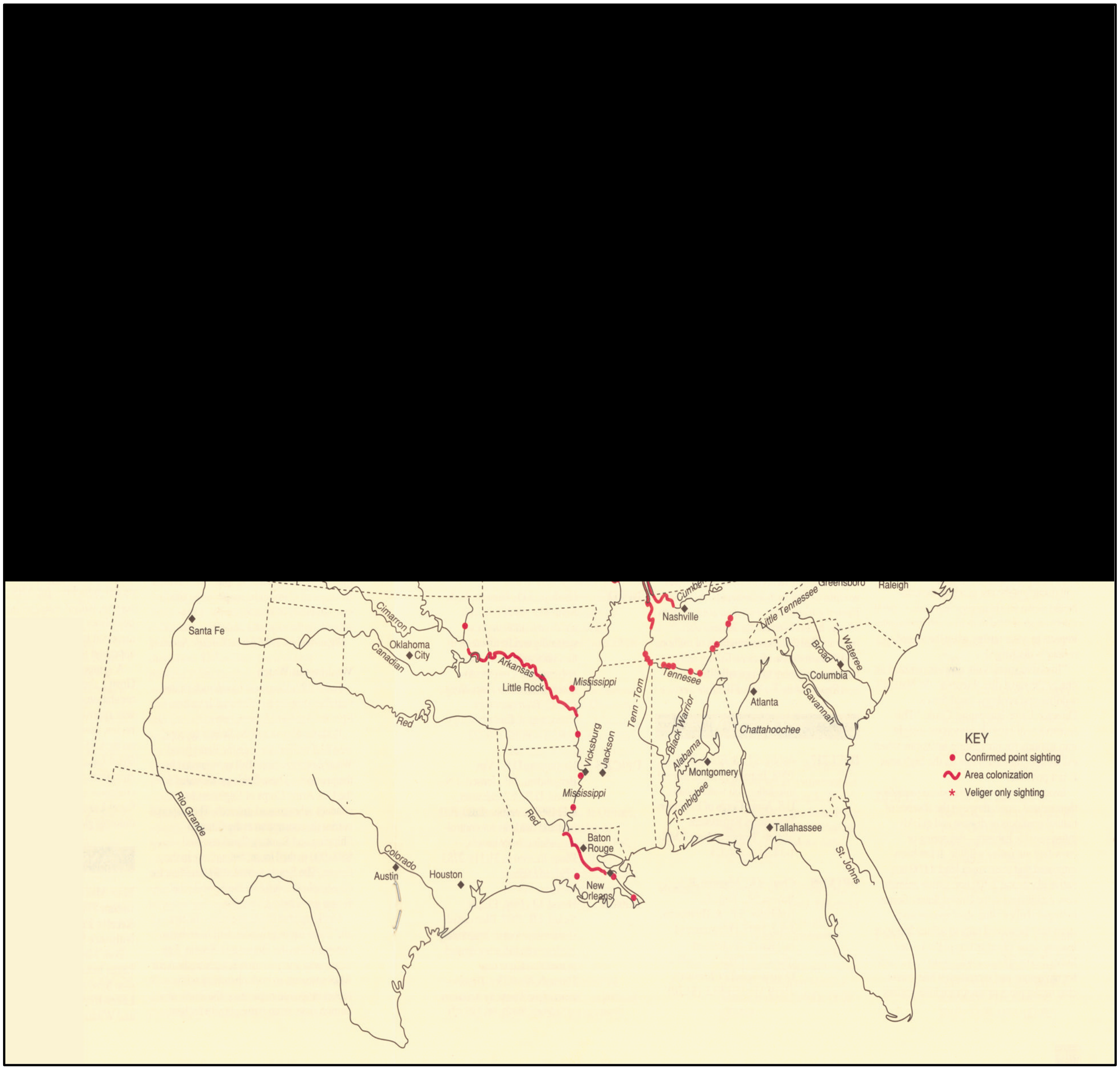

Figure 1. Zebra mussel distribution (from *Dreissena!*, Vol 9(3), Summer 1998, 8-9, courtesy of New York Sea Grant) (for a current version of the map please see: *http://www.cce.cornell.edu/seagrant/nansc/zmaps.htg*)

effort to identify more compounds that will be effective against zebra mussel. While oxidizers, and particularly the various forms of chlorine, continue to be the most commonly used of the chemical controls, additional compounds have been registered; and more continue to be tested in the search for environmentally sound and effective treatment of this pest.

Chemical applications can be used for both proactive treatment, to ward off settlement of zebra mussels and subsequent fouling before they occur, and for reactive treatment, where clean-up measures are used to remove zebra mussels already at nuisance levels and disrupting system function. It has been suggested that reactive systems or procedures are adequate if 1 year's worth of shell buildup and fouling can be tolerated by the system, allowing for the minimum of an annual purging (Claudi and Mackie 1994). Both oxidizing and nonoxidizing chemicals are suitable for this type of application. Where macrofouling buildup or the "legacy" problems of disposal of dead mussels and shells (Allen 1994) cannot be tolerated, however, proactive treatments of nonoxidizing chemical are more commonly used. These create environments hostile to the settlement stage of the zebra mussel larvae (the veliger) and maintain inviable conditions that prevent adult zebra mussel translocation and settlement. Both approaches can be combined into a single strategy.

The goal of any chemical control program is to choose chemicals that will be effective, work rapidly, and have a minimal environmental impact. Treatment chemicals can be categorized as oxidizing (electron acceptor) and nonoxidizing compounds, with different properties and requirements. Since these groupings also generally differentiate between nonproprietary versus proprietary and organic versus inorganic compounds, they are followed in this guide to describe the chemistry of molluscicide compounds and give directions for the use of each compound. Further guidance for designing a control program using chemical molluscicides for a facility or installation is given by Claudi and Mackie (1994). They provide a detailed description of chlorination strategies and outline criteria for effective chemical application in general.

Oxidizing Molluscicides

Several compounds with toxic biocidal oxidizing activity that are already widely used as disinfectants in treatment of drinking water and wastewater and in power plant facilities to remove slime and biofilms are highly effective on zebra mussels. The environmental effects and requirements for safe discharge are well understood by users and regulators. While oxidizers present problems because of their corrosive effects on metals, their low cost makes them very attractive in mussel control programs.

The major types of oxidants frequently used for chemical control of biofouling and available as generic chemicals for molluscicide use are listed in Van Benschoten et al. (1993):

a. Chlorine (gas, liquid sodium hypochlorite, powdered calcium hypochlorite).

b. Chlorine dioxide (ClO_2).

c. Chloramines, such as monochloramine (NH_2Cl).

d. Ozone (O_3).

e. Hydrogen peroxide (H_2O_2).

f. Bromine.

g. Permanganates (MnO_4^-), such as potassium permanganate.

In general they have similar modes of action based on the oxidation of organic matter, which leads to toxic and lethal effects. They are suitable for use in preventative treatment, where they are added to a system throughout the breeding season at from 0.1 to 0.5 mg L^{-1} (ppm) total residual oxidant (TRO) to prevent settling. For reactive treatments, continuous application of 0.5 to 1.0 mg L^{-1} TRO for 2 to 4 weeks can eliminate established adult colonies, but concentration and contact time required depends on temperature, water chemistry, and physiological state of the zebra mussels. Mussels do detect oxidants, and shell closure for up to 2 weeks may reduce efficacy in adults (Claudi and Mackie 1994).

While chlorine dominates all chemical use for zebra mussels, there has been concern that there will be additional restrictions on its discharge in the future due to its nonselectivity and its formation of undesirable by-products such as trihalomethanes (THMs) and chloramines upon coming into contact with organic compounds in open water. This will change the picture for chemical control of zebra mussel. Dechlorination can be achieved by addition of sodium sulfite (Barton 1993). While ozone and hydrogen peroxide are not dealt with in this user guide, toxicity to zebra mussels is summarized by Electric Power Research Institute (EPRI) (1993).

Nonoxidizing Molluscicides

Most of these chemicals were originally developed for bacterial disinfection and algae control in water treatment systems (Claudi and Mackie 1994). They include organic film-forming antifouling compounds, gill membrane toxins, and nonorganics. The proprietary formulations have a higher per-volume cost than oxidizing chemicals but remain cost-effective due to lower use rates and rapid toxicity. They often can provide better control of adult mussels due to the inability of mussels to detect them; because shells remain open, shorter exposures are required. Most are easy to apply and do not present corrosion problems for metal components. Although most compounds are biodegradable, detoxification or deactivation may be required to meet State and Federal discharge requirements; but there is virtually no formation of toxic by-products (McMahon, Shipman, and Long 1993).

Intermittent, periodic, or semicontinuous applications rather than continuous applications of nonoxidizing compounds for adult mussel control adds to their cost-effectiveness (Netherland 1997). Usually treatment is on a periodic basis for 24 hr or less during the warm-water season to remove newly settled mussels or adults, with two to three applications per year: early in the season, at peak veliger activity, and when evidence of settlement is first seen. If they are used in coordination with monitoring programs that provide accurate veliger and mussel settlement data, frequency of application can be minimized (Green 1995). Water temperature helps determine treatment concentration and length of exposure required (Claudi and Mackie 1994; Green 1995).

Within the nonoxidizing molluscicides there are several groups of compounds:

a. *Quaternary ammonium compounds, polyquaternary ammonium compounds, or polyquats*. Quaternary ammonium compounds (QACs) are organic salts that have a wide variety of uses in industry. They have been used as coagulants and flocculants in potable water since the late 1960's, and have American National Standards Institute/National Sanitation Foundation (ANSI/NSF) Standard 60 (1997) certification for this use. Several of these have been used for control of Asian clam (*Corbicula fluminea*). They are also effective in controlling mollusk fouling in once-through industrial cooling systems, and recently received Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)/USEPA registration for use as molluscicides in municipal water (Blanck, Mead, and Adams 1996). QACs are cationic surfactants, and it is their surface-binding activity that produces antifouling biocidal effects. Two major types of chloride-ion-containing QACs are used commercially in the molluscicides CLAM-TROL CT-1™ and MACROTROL™ 9210 and Calgon H-130M, and BULAB® 6002 contains a poly-QAC (polyquat) (EPRI 1993). QACs also adsorb strongly to sediments, clay particles, organic matter, and other negatively charged surfaces, so that water column concentrations are normally very low (EPRI 1993). Where QACs are released directly into a receiving system, they may require detoxification by adsorption onto bentonite clay or other agents, but are not harmful to aquatic organisms once they are bound to anionic substances (Dobbs et al. 1995).

b. *Aromatic hydrocarbons*. Compounds such as BULAB® 6009 and MEXEL 432™ also have molluscicide properties due to their surfactant and anti-macrofouling activity.

c. *Endothall*. This herbicidal compound, long used against aquatic nuisance plants, has been formulated as EVAC® and registered to control zebra mussel.

d. *Metals and their salts*.

   (1) Copper ions have long been known to be toxic to planktonic or microbial organisms in water, and yet not pose a threat to humans due to binding and inactivation in sediments. These properties are put to use in the deployment of copper ions via the MACROTECH system for zebra mussel control. Various copper and zinc ions are major components of antifouling coatings and chemicals (Race and Kelly 1997).

   (2) Potassium, potash, and potassium chloride have flocculant activity that is able to precipitate various life stages of the zebra mussel out of water (Fisher et al. 1991).

The Use Guide Outline

In the following chapters of this guide, each molluscicide compound is described using the topics in the following format. Here, the topics are introduced with general information and definitions of terms related to how the compounds are used. Refer to these definitions when assessing the guidelines for individual compounds. Many of these concepts are further defined and discussed by Claudi and Mackie (1994).

The source of information on individual compounds has been primarily the product label and its Materials Safety and Data Sheet (MSDS). Both of these documents are available from the manufacturer or vendor (and may be posted on the Internet), and are required by law to be in the possession of the user at the time of molluscicide use.

Chemical Name and Formulations

This topic gives the compound name, brand name of proprietary or commercial formulation, and manufacturer or supplier. Where compound is generic, e.g., chlorine, no supplier is given.

Mode of Action

This topic describes the way in which the compound acts against mussels to produce a toxic or inhibitory effect.

Application Strategies

Typical systems for applying chemicals to systems and sites usually require specific chemical feed equipment, piping for chemical transport, diffusors to introduce chemical to the water, and areas for chemical storage or generation (Lawrence 1997). A variety of treatment timings can be used. Claudi and Evans (1993) summarize them as *reactive* strategies, used after zebra mussels have become established in a raw water system or have fouled external structures, and *proactive* strategies designed to prevent settlement:

a. *End-of-season*. Targets adult mussels. Chemical is applied for a period sufficient to kill all adults established in the system at the end of the breeding season; thus, the system must be able to tolerate one season of fouling. Oxidizing or nonoxidizing chemicals may be used. Oxidizing chemicals are expected to require dosing at high levels for at least 2 weeks to overcome mussel closure. Ten to twenty percent of individuals are expected to survive, and prolonging treatment to achieve 100 percent mortality may be impractical.

b. *Periodic*. Targets adult mussels on a regular basis; usually carried out when densities and size of adults remain low, so that debris removal is lessened. System must be able to accept some macrofouling. It is not necessary to achieve complete (100 percent) mortality. Oxidizing or non-oxidizing chemicals can be used.

c. *Ongoing intermittent/(continuous pulse)*. Low levels of chemicals target postveligers to prevent infestation. Since postveligers are more susceptible than adult mussels, lower concentrations can be used; however, these will then not control established adults. For use in clean systems where no plugging can be tolerated (e.g., thin piping). Little debris produced.

d. *Continuous*. To discourage all postveliger settling. For use where there is no tolerance of obstruction or fouling; lower concentrations can be used but they must be constant. Established adults affected only if chemical applied all season. Carried out only with oxidizing chemicals.

Treatment strategies also involve the type of application and the extent of the system treated at any one time. There are several options, depending on the system configuration and location of current or potential problems:

a. *Entire raw water treatment*: Addition of chemical to the forebay or injected into suction or discharge of system pump piping.

b. *Entire system treatments*: Addition of chemical so that it is present and circulating in all water within the operating system.

c. *Forebay treatments*: Treatment of water in a holding area before it is brought into the main operating system.

d. *Targeted treatments*: Addition or application of chemical to only certain portions of the complete operating system or parts of multiple systems.

e. *Recirculation treatments*: Treat forebay, then isolate forebay from incoming water and recirculate through system.

Where applicable, closed-loop systems may be set up to reduce the amount of chemical needed per application.

Timing of Application

The efficiency of many strategies is enhanced if their timing is coordinated with veliger and mussel settlement data collection.

Generally, chemical controls to prevent settling and infestation need to be only over spawning periods, defined as water temperatures greater than 55 to 61 ºF (12 to 16 ºC). Continual application of molluscicides is recommended at this time for maximum effectiveness in intake structures (McMahon and Tsou 1990).

a. *Off-line*: While a system or portion of a system is not in operational mode.

b. *On-line*: While a system is functioning.

Application Rates

A wide range of concentration/exposure time combinations can be effective. Many are reported in the literature and in product information, but much is still being found out on a trial and error basis.

Maximum Water Concentration

The Clean Water Act requires that registered biocides discharged to waters of the United States from a point source must be regulated such that water quality-based effluent limits (WQBELs) for that biocide are established in a National Pollutant Discharge Elimination System (NPDES) permit to meet State water quality standards. There must also be compliance with each State's Antidegradation Policy. Thus, discharge limits of the chemical control compound depend on local, State, and Federal water restrictions as permitted under the NPDES program to regulate the amount of pollutants that may be discharged to waters by each discharger. Effluent guidelines are technology-based and are usually given on a case-by-case basis for individual facilities.

While commercial molluscicide labels may include specific NPDES discharge limits for that compound, many labels point out that the user must obtain an NPDES permit from the appropriate State/Tribal agency or USEPA Regional Office and comply with State water quality requirements.

Products registered as pesticides by the USEPA must be handled and applied within the limits of the label instructions.

Although most molluscicides are biodegradable, some detoxification or deactivation may be required to meet State and Federal discharge requirements. See the topic "Adjuvant/Detoxicant/Deactivant Use."

Use Restrictions

Discharge restrictions and limitations on downstream use of treated water are discussed under this topic, along with permit requirements.

Timing of Results

This topic describes how rapidly zebra mussels are affected. Monitoring may be required (see "Field Instructions and Guidance on Operational Applications").

Toxicological Data

Signal Word: The USEPA-assigned signal word indicates approximately how toxic a pesticide product is. Products that are highly toxic must display on the label the signal words DANGER-POISON along with a skull and crossbones symbol. Products that display only the signal word DANGER are corrosive and can cause irreversible eye damage or severe skin injury. Products that display the signal word WARNING are moderately toxic or can cause moderate eye or skin irritation. Products that display the signal word CAUTION are slightly toxic or may cause slight eye or skin irritation.

Aquatic toxicology: Data for the effects of the compound on various freshwater organisms. Aquatic toxicity levels are usually reported as LC_{50}, which is the concentration lethal to 50 percent of test organisms.

Precautions

This topic gives pertinent information on precautions to take when handling the compound in its undiluted and dilute states. Also refer to MSDS for personal protective equipment information.

Field Instructions and Guidance on Operational Applications

It is recommended that before a full-scale application of a treatment or treatment system, an onsite performance test be run incorporating site conditions of water temperature and chemistry and other local conditions. These factors will affect molluscicide performance (Allen 1994).

Optimal timing and efficacy of chemical control treatments can be determined using biobox monitors set up in various configurations to test presence or settlement of veligers. These are chambers connected to a side stream of the water system that allow sampling of incoming veligers or determination of toxicity to adults preseeded into the boxes. Molluscicides can be injected into the water supply at a point midway between two side-stream monitors at preestablished time intervals to evaluate treatment efficacy (Claudi and Mackie 1994; Green 1995). Data collected before, during, and after application will show effect of treatment.

Adjuvant/Detoxicant/Deactivant Use

Although most molluscicides are biodegradable, some detoxification or deactivation may be required to meet State and Federal discharge requirements. Deactivation compounds may be recommended or be required by the label during molluscicide use or before discharge.

Proprietary deactivants or detoxicants are available. Bentonite clay in a dry or slurry form is a standard agent for several of the nonoxidizing compounds, added to the system discharge upstream of its outlet to the environment. Binding properties of the clay generally render the biocide inactive.

Application Techniques

This topic gives special instructions for adding the compound to the system and maintaining it.

Antidote Information

This topic gives brief emergency instructions, including phone numbers for companies that can supply treatment information.

References

Technical references for additional information are provided for each molluscicide.

Additional Chemicals

Numerous pesticide compounds in addition to the ones presented in this guide have been suggested or investigated for zebra mussel control and are discussed in a variety of research and product information literature. However, most are currently not in common use, either because they are less effective on zebra mussels, harmful to native bivalves as well as zebra mussel and therefore limited to use in contained systems (Claudi and Mackie 1994), or have not yet been registered for zebra mussel control. Although USEPA regulations may allow use of pesticide compounds in sites where they are registered (see next section), efficacy data should be consulted before any of these are used. Some pretreatment chemicals have been studied, such as the use of carbon dioxide before chlorination to narcotize the bivalves and cause them to "gape" (Elzinga and Butzlaff 1994).

Some of the proposed compounds are given in the following tabulation, along with their primary use.

Proprietary Compounds Proposed for Zebra Mussel Control but Not in General Use

Compound (Trade Name)	Chemical Name	Use	Reference
Clonitralid	5-chloro-n-(2-chloro-4-nitrophenyl) -2-hydroxybenzamide compound with 2-aminoethanol (1:1) (9ci)	Molluscicide Lampricide	
Niclosamide (Bayluscide 70)	2-aminoethanol salt of 2',5-dichloro-4',nitro-salicylanilide	Molluscicide Larvicide	
Bayer 73 (Bayluscide)	2',5-dichloro-4',nitro-salicylanilide	Lampricide	Fisher et al. 1994 Waller et al. 1993
Penaten®	Zinc oxide	Antifouling	Magee, Wright, and Setzler-Hamilton 1997
Rotenone (Noxfish)	1,2,12,12a-tetrahydro-2-iso-propenyl 8,9-dimethoxy-[1]bensopyrano-[3,4]furo [2,3-b] [1] benzo pyran-6 (6aH) one	Piscicide	Fisher et al. 1994
Salicylanilide I (Sal I)	2',5-dichloro-3-*tert*-butyl-6-methyl-4'-nitrosalicylanilide		Fisher at al. 1994 Waller et al. 1993
TFM (Lamprecid)	3-trifluoromethyl-4-nitrophenol	Lampricide	Fisher et al. 1994 Waller et al. 1993

A number of compounds derived from natural sources such as plant toxins have been tested for use in controlling zebra mussels (Taylor and Zheng 1995, 1997). In addition, antibiotic materials excreted by other aquatic organisms to keep them free of biofouling are relatively common, and these are being investigated for their ability to prevent settling when applied as extracts or as a component in coatings. However, none of these has become commercially available yet. Compounds that are toxic to mussels are also potentially toxic to other life forms, and they must be tested and handled as carefully as other molluscicides.

One such natural compound, Endod, is a plant toxin product that includes chemicals called Lemmatoxins derived from the fruit of the African soap berry tree *Phytolacca dodecandra*. Two U.S. patents for its use as molluscicides have been awarded. Lemmatoxins have been shown to be lethal to zebra mussels at concentrations higher than 15 mg L^{-1}, while lower concentrations inhibited attachment and aggregation of adult mussels (Lemma et al. 1991; Lee, Lemma, and Bennett 1993). Toxicological studies have been done on nontarget mammals (Hietanen 1997).

USEPA Registration of Chemical Molluscicides

An understanding of the regulatory and legal standing of pesticide compounds such as molluscicides can be useful in handling these products. Howe et al. (1994) and Burns (1994) describe how FIFRA, enacted in 1972, relates to the registration and use restrictions of chemicals for zebra mussel control. The act monitors chemicals intended for control of living organisms and, as amended, requires registration and reregistration by the USEPA of pesticides sold or used in the United States to ensure that they will not cause unreasonable risk to the environment or human health when used according to the label directions. These regulations then apply to anyone who manufactures, formulates, markets, distributes, uses, or disposes of pesticide products, including aquatic biocides.

The primary registration mechanism is governed by FIFRA Section 3. Applications for registration of molluscicides may be for new active ingredients, the new use of a previously registered pesticide, or chemicals similar to currently registered compounds. The registration process (paid for by the registrant) is not inexpensive or fast because it requires detailed research by the registrant to determine the efficacy and environmental side effects of the active ingredient. Some of this testing is carried out via Experimental Use Permit (EUP) provisions under FIFRA Section 5. This may delay or prevent approval for use of the compound in a specific state. Most states require their own specific registration of pesticides in addition to registration with the USEPA. The expense of acquiring registration for biocidal compounds has understandably slowed the proposal and marketing of new chemicals specifically for the small area of zebra mussel control.

The effect of discharge of water containing molluscicidal chemicals on downstream receiving waters must be considered prior to the formulation of a treatment program. Even with discharge limits and requirements and the use of deactivation, there may be an effect on the ecosystem that needs to be avoided or restricted to certain times of the year (Claudi and Evans 1993). The legislation currently used to control direct discharges to waters of the Nation is the NPDES permit program. This was made possible by the passage of the Federal Water Pollution Control Act

Amendments of 1972 (also referred to as the Clean Water Act). These permits place limits on the amount of pollutants that may be discharged to waters by each discharger. These limits are set at levels protective of both the aquatic life in the waters that receive the discharge and human health. The Clean Water Act requires that registered biocides discharged to waters of the United States from a point source must be regulated such that WQBELs for that biocide are established in an NPDES permit to meet State water quality standards. There must also be compliance with each State's Antidegradation Policy. Thus, one of the label requirements for use of many aquatic biocides and pesticides in aquatic environments is to obtain an NPDES permit from the appropriate State/Tribal agency or USEPA Regional Office and to comply with State water quality requirements. Lack of a permit could result in enforcement action under FIFRA and the Clean Water Act. A risk-benefit analysis is also carried out by the USEPA, and a pesticide can be designated for "restricted use" if it is judged as presenting a high risk to humans or the environment. States usually require these chemicals to be applied only by certified applicators or people in their employ.

As well as FIFRA Section 3 registration, conditional use of pesticides may be authorized through Special Local Needs under Section 24(c); through Emergency Exemptions (ee) (Section 18); or through EUP provisions under Section 5. Use of a registered product on a pest not listed on the product label is allowed under Section 2(ee) as long as application is to a site stated on the label (Howe et al. 1994). However, specific registration for use in once-through cooling systems is required in many water handling operations where mussels are treated in these areas (Claudi and Mackie 1994).

It is important to remember that the product label of a registered pesticide is a legal document. Use of an aquatic biocide or molluscicide in a way that is inconsistent with the instructions provided on the label is a violation of FIFRA and can result in civil or even criminal action, via proceedings from the USEPA under FIFRA or from certain states (Howe et al. 1994). Compliance with the National Environmental Policy Act (NEPA) is required if Federal funds are used for zebra mussel control. This legislation dictates that control methods used at public facilities must not negatively affect native biota or existing water quality (Miller et al. 1992). A protocol for compliance with the NEPA process that should used in developing chemical control strategies for zebra mussel is described by Miller et al. (1992), and a working plan is reported on by Tippit, Cathey, and Swor (1993).

Sources of Additional Information

Dreissena! This newsletter is published six times per year by the National Zebra Mussel and Aquatic Nuisance Species Clearinghouse and presents the most current information and summaries of research, meetings, legislation, and sightings of zebra mussels (*http://www.entryway.com/seagrant/products.cfm#newsletters*). The Clearinghouse has a Web site at *http://www.entryway.com/seagrant/* .

Sea Grant Nonindigenous Species Site (SGNIS): *http://www.ansc.purdue.edu/sgnis/*

USGS Zebra Mussel Information Sources: *http://www.fcsc.gov/zebra.mussel/*

The U.S. Army Engineer Research and Development Center Zebra Mussel Research Program: *http://www.wes.army.mil/el/zebra/zebra.html*

The Zebra Mussel Information System (ZMIS) CD-ROM: *http://www.wes.army.mil/el/zebra/cd.html*

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2 Chlorination

The cost-effective oxidizing activity of chlorine has made it the most commonly used compound for all types of water disinfection and biofouling control in North America, and it has been used in potable water treatment since the beginning of the 1900's (Van Benschoten et al. 1993). Chlorination, primarily via sodium hypochlorite, has dominated the chemical control of zebra mussel in both Europe and North America, and remains the least expensive and most popular method of removal. Chlorination effects can be provided by a range of compounds—the hypochlorites of sodium, potassium, or calcium; chlorine and chlorine dioxide gases; and sodium chlorite—and their toxic properties can be used to control zebra mussels and related nuisance mollusk species. Chlorine is able to kill or prevent settling of planktonic veliger larvae in raw water piping systems. In general, chlorine treatment for zebra mussel control should be applied at the most suitable time, for the shortest period, and at the lowest concentration to be efficacious (Jenner and Janssen-Mommen 1993). However, adult mussels will close at concentrations of from 1 to 2 mg L^{-1} and remain closed for up to 2 weeks.

Claudi and Mackie (1994) discuss chlorination processes for zebra mussel control in industrial systems in detail, along with its pros and cons, and Netherland (1997) gives a brief summary of chlorine usage. Chlorine has a number of important advantages: it is relatively inexpensive, it works in most raw water systems, it is toxic at low concentrations and quickly loses toxicity without bioaccumulating, and it can be applied with simple mechanisms. However, there are several drawbacks to the chlorination process. The transport and storage of gaseous or liquefied chlorination products involve hazards, and their corrosive properties can harm system components, so that they all require special handling. Discharge also presents problems because carcinogenic compounds known as trihalomethanes may be formed where organic compounds are present in water. AOX (adsorbable organic halides) may also be formed, but do not present risks. Differences in water quality may incur extra costs where discharge concentrations may be unpredictable due to varying chlorine demand.

There has been concern that the cumulative effects of extensive chlorine use for zebra mussel control in large rivers in North America could be problematic due to toxicity to nontarget organisms and formation of trihalomethanes. Although chlorine discharge into natural water bodies is already regulated, it is possible that it may be prohibited or severely restricted in the future if usage increases significantly (Claudi and Mackie 1994). However, to date, these products provide the most effective and low-cost control in the majority of situations.

The next section reviews the general properties of chlorination via hypochlorite and chlorine gas; additional chlorine oxidizers (chlorine dioxide, sodium chlorite) are discussed separately.

Hypochlorite and Chlorine Gas

Chemical Names and Formulations

Chlorination compounds are available from numerous commercial sources as the following chemicals:

a. Calcium hypochlorite, $Ca(OCl)_2$; solid.

b. Sodium hypochlorite, NaOCl; liquid.

c. Potassium hypochlorite, KOCl.

d. Chlorine, Cl_2; gas.

Mode of Action

Chlorine controls zebra mussels through the effects of oxidation, consisting of either direct toxic effects on the adult, inhibition of settlement and growth of the larval stage, or weakening of the byssal thread attachments. Toxicity of chlorine to zebra mussels is a function of concentration, exposure time, and the type and quantity of chlorine compounds formed in water following treatment (Claudi and Mackie 1994).

Chlorine or hypochlorite reacts with water to form hypochlorous acid (HOCl), which readily dissociates to hydrogen ions (H^+) and hypochlorite (OCl^-). The hypochlorite ion is reduced to chloride ions and hydroxide ions forming a basic solution as it accepts electrons:

$$OCl^- + 2e^- + HOH \rightarrow Cl^- + 2\,OH^-$$

The ratio of hypochlorous acid to hypochlorite ions depends mainly on pH and to a lesser degree on temperature. Together, the two make up *free available chlorine* (FAC). The undissociated hypochlorous acid (HOCl) is a strong oxidizing agent and has the principal biocidal activity of these two chlorine species, damaging membranes, diffusing through cell walls, and disrupting enzyme activity, and perhaps affecting ion regulation (Claudi and Evans 1993; Claudi and Mackie 1994).

These FAC compounds react with ammonia and other nitrogen-containing compounds to make chloramines, which also contribute to disinfection and are known as combined available chlorine. These two types of available chlorines make up total residual chlorine (TRC) (Van Benschoten et al. 1993; Claude and Mackie 1994). The presence of organic nitrogen and other compounds reduces TRC because chlorine forms complex nitrogen compounds. Additional chlorine has to be added to obtain a specific TRC level, and this differential, called chlorine demand, varies with type of raw water and season.

Chlorination affects zebra mussels through toxic effects of free chlorine and chlorine products. It affects adults, inhibits settlement and growth of veligers, and weakens the byssal thread attachments that hold the mussels in place. Because mollusks sense chlorine at 0.04 mg L^{-1} total residual oxidant and close for extended periods to escape it, it is thought that oxidizing biocides can cause mussel mortality through asphyxiation or limited glycolysis over a prolonged period of constant chemical feed. In addition, the free chlorine and chlorine products have a chronic toxic effect. The toxic oxidant compound is also thought to accumulate as some siphoning goes on (Van Benschoten et al. 1993, 1995).

Application Strategies

End-of-season treatment. This treatment is given to flush out relatively small amounts of accumulated adults. Debris can be a problem; end-of-season (November) chlorination is not optimal if this is the only treatment or chemical being used.

Periodic treatment. This consists of at least three treatments of several weeks length; if given over the breeding season (May to November), adult mussels will be eliminated. Less debris is generated, as mussels are smaller.

Intermittent treatment. This treatment is useful for prevention of new primary veliger settlement, especially where adult mussels cannot be tolerated. However, it is not effective against established adults. It can be combined with an out-of-season continuous chlorination treatment to eliminate adults.

Semicontinuous. Frequent on/off cycling of treatment can have effects similar to continuous chlorination in keeping zebra mussels in a stressed status of shell closure. This treatment has a lower cost of material due to reduced exposure time.

Continuous. Constant presence of chlorine at low levels can prevent veliger settling and survival.

Chlorinating compounds can be added to water as gas (Cl_2), liquid (e.g., NaOCl), or solid (e.g., calcium hypochlorite, $Ca(OCl)_2$). Due to difficulty and hazard of handling pressurized chlorine gas, the majority of applications are of liquid hypochlorite. Various concentrations of sodium hypochlorite are available, with 12 percent active chlorine by weight being most commonly used by industry (Claudi and Mackie 1994). Chlorine gas requires potable water supply for maintenance and operation of a gaseous chlorine system, and air scrubbers to filter exhaust.

Timing of Application

If a single long-term application is being used to kill all mollusks present, it should be made following the reproduction period to ensure that no additional veliger settling will occur. Reproduction in zebra mussel is also dependent on water temperature, and this timing will be keyed in to the time of year.

A one-time application of this kind can be done if infestation is low enough that killed material will flush out without blocking the system. If infestation is greater and may block any parts of the system, twice-a-year chlorination may be required.

Winter treatment with low levels of chlorine may be useful for ridding systems of adult zebra mussels, although the process is slow (Van Benschoten et al. 1993).

For veliger control there is no need to chlorinate during winter when temperatures are too low for mussel reproduction, and chlorination can be suspended during periods when veligers are not present in intake water (Payne and Lowther 1992; Claudi and Mackie 1994)

Application Rates

Concentration and exposure time. Control of zebra mussel depends upon chlorine concentration, contact time, and water quality and temperature, where the relationship between concentration and exposure time is usually an inverse one. Van Benschoten et al. (1993, 1995) give models for predicting 95 percent mortality as a function of temperature and total residual chlorine concentration. Generally, the contact time required decreases as concentration increases; however, reducing chlorine concentrations by half results in half the mortality in less than twice the contact time, and this may be a way to reduce chemical costs (Van Benschoten et al. 1993). Water temperature is an important factor in effectiveness of chlorination in zebra mussel control; since chlorination is usually held at ambient temperature at treatment sites, the seasonal timing of chlorine application is important (Claudi and Mackie 1994). Higher concentrations of chlorine are required at lower temperatures in order to be equally effective. Chlorination may not be practical at less than 50 ºF (10 ºC), due to the longer contact time required.

Chlorine demand. Chlorine demand of incoming water should be established and included in calculating the application concentration. A guide to these calculations is given in Claudi and Mackie (1994). Consider effects of pH, organic and inorganic nitrogen content, temperature, and physiological status of zebra mussels on concentrations required for effective treatment. Water with large amounts of organic and inorganic compounds has high chlorine demand. Most of this information given here comes from experience with Great Lakes water; results may differ with other water qualities (Claudi and Evans 1993).

Mortality. Generally, 0.5 mg chlorine L^{-1} (ppm) for 2 hr gave 100 percent mortality in veligers (Klerks, Fraleigh, and Stevenson 1993). Fatality in adult mussels occurred at concentrations of 2.0 mg L^{-1}.

End-of-season treatment. While chlorination is not the most efficient method where a single annual application is used to eliminate established adult mussels, it can be used in this way by applying high doses continuously for 2 to 3 weeks. Results from tests in the field (Claudi and Mackie 1994) are shown in the following tabulation.

Mortality with End-of-Season Chlorine Treatment		
Chlorine Concentration mg L^{-1}	**Exposure Time weeks**	**Mortality percent**
0.5	2	95
1.0	9	100
1.5	7	100
2.0	3	90
2.0	6	100

Periodic. Similar results will be produced by the treatment levels used in single end-of-season applications (Claudi and Mackie 1994). Other research (McMahan and Tsou 1990; Jenner and Janssen-Mommen 1993) is summarized in the following tabulation.

Mortality with Periodic Chlorine Treatment		
Concentration mg L^{-1}	**Exposure Time days**	**Results % kill**
0.5	7	75
0.3	>14 to 21	> 95
0.5 TRC or 0.5 TRO[1]	14 to 21 at 20 to 25 ºC (68 to 77 ºF)	> 95
[1] Total residual oxidant.		

Intermittent. Intermittent treatment, used throughout the breeding and settlement period at rates of 2 mg L^{-1} chlorine (TRC) for half-hour periods at 12-hr intervals, has been effective in preventing primary veliger settlement but not in removing established adults (Claudi and Mackie 1994). Such a treatment can be combined with an out-of-season continuous chlorination treatment for 2 to 6 weeks at 2 mg L^{-1} TRC to eliminate accumulated adults (Claudi and Evans 1993). Treatment combinations are shown in the following tabulation.

Mortality with Various Concentration, Exposure, and Interval Combinations of Intermittent Treatments				
Concentration	**Exposure min**	**Interval hours**	**Mortality**	**Reference**
0.8 % 0.5 mg L^{-1} TRC	30	12	100 % veliger No settlement	Barton 1993
2 mg L^{-1}	30	12	No new veliger settlement	Claudi and Evans 1993

Semicontinuous. On/off cycling of chlorine over short intervals takes advantage of the lag time of mussel shell opening after treatment is discontinued to mimic continuous treatment while reducing total residual oxidant loading significantly. It is expected to be comparable to continuous treatment in effects, but with lower chemical use and discharge, and subsequently lower cost. Tests showed that a cycle of 15 minutes of 0.5 ppm chlorine followed by 30 minutes without chlorine reduced settling to levels found with continuous treatment (Claudi and Mackie 1994). Results are summarized in the following tabulation.

Mortality with Semicontinuous Cycling		
On/Off Cycle min	**TRC Concentration**	**Live Mussels on Surface**
15/15	0.5	12
15/30	0.5	2
15/15	0.3	64
Untreated Control	0	4,993

Continuous. Low, sublethal levels of chlorination may be effective against zebra mussel by eventually producing chronic toxicity or preventing macrofouling. Speed of water flow may affect how readily mussels are detached and swept away. Continuous treatment at 0.5 mg L^{-1} TRC has been successful, preventing new settlement and killing adult mussels regardless of speed of flow (Claudi and Mackie 1994). The following tabulation shows several rates.

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Mortality with Continuous Treatment			
Concentration mg L^{-1}	**Exposure days**	**Results**	**References**
0.5	90	100% Prevented all new settlement	Claudi and Evans 1993
0.3	90	100% Prevented all new settlement	Claudi and Evans 1993
0.3 to 0.5	14 to 21	100%	Miller, Payne, McMahon 1992

Maximum Water Concentration

Discharge limits for specific facilities depend on local, State and Federal water restrictions as permitted under the National Pollutant Discharge Elimination System program.

For power plants greater than 25 MW, the U.S. Environmental Protection Agency effluent limitation guideline for chlorine is 0.2 mg L^{-1} (ppm) TRC (Federal Register, 40 CFR Part 423, November 1982). This discharge concentration is limited to 2 hr per day unless the need for use in combating macrofouling is demonstrated (Jenner and Janssen-Mommen 1993).

Other discharge configurations may be permitted. For example, the Perry Nuclear Power Plant, North Perry, Ohio, has a regulatory discharge limit for chlorine of maximum daily discharge time of 2 hr, with concentration limits of 0.2 mg L^{-1} for a 30-day average and 0.5 mg L^{-1} on a daily basis (Barton 1993).

Use Restrictions

Production of trihalomethanes must not exceed 80 ppb (Fg/L) in drinking water (U.S. Environmental Protection Agency 1994). Prior to this, the standard was 100 ppb.

Timing and Appearance of Effects

Considerable lag times between application and adult zebra mussel death have been observed, presumably due to shell closure when the presence of oxidant is sensed. Lag times of from 2 to 18 days are noted and generally decrease as chlorine concentration increases (Van Benschoten et al. 1993).

Resistance to chlorine can vary with age, size, and developmental stage of the mussel, with older and larger individuals being more resistant; veligers are much more susceptible than adults (Claudi and Mackie 1994).

Toxicological Data

Toxicology of sodium hypochlorite for two important aquatic species is shown in the following tabulation:

Aquatic Toxicology of Sodium Hypochlorite (NaOCl): 5% Active Chlorine Solution[1]		
Species	**Test**[2]	**Concentration mg L^{-1}**
Rainbow trout	48-hr LC_{50}	0.07
Fathead minnow	96-hr LC_{50}	5.9

[1] From Materials Safety and Data sheet (ACROS Organics 1996).
[2] Concentration lethal to 50 percent of the individuals.

Sodium hypochlorite is broken down in the environment into sodium chloride, oxygen, and water. Other substances may be formed to a limited extent. These by-products are often referred to as AOX (adsorbable organic halides). A great many studies have been made to provide a risk assessment of NaOCl in terms of its formation of AOX. It was concluded that the amount of AOX is very small both in absolute terms and relative to other human activities and natural sources. The majority of these compounds are easily degradable and are primarily water soluble and not bioaccumulative. Highly chlorinated species, such as dioxins, are not formed.

Precautions

Possible by-products from antifouling chlorination may include chlorobromoform, halogenated benzenes, and phenols (Jenner and Janssen-Mommen 1993).

Sodium hypochlorite is corrosive and causes burns to eyes, skin, and internal organs if ingested or inhaled.

When handling sodium hypochlorite, wear rubber gloves and splash shield.

Chlorine gas presents risk of potentially dangerous leaks. Extensive safety training may be required for those handling the material and for any response team.

Field Instructions and Guidance on Operational Applications

Store sodium hypochlorite solution away from heat and light to prevent decomposition, such as in polyethylene tanks vented to release oxygen. Provide containment basins. Avoid use of stainless steel in storage or handling. If dilution is required prior to treatment, use only deionized or distilled water.

The standard industrial strength 12 percent solution of sodium hypochlorite can precipitate calcium carbonate ($CaCO_3$) where raw water contains high levels of calcium. Allow for this by avoiding small-diameter piping, etc.

To monitor residual chlorine, most agencies and industries analyze for chlorine using automatic on-line or laboratory testing based on the amperometric (electrochemical) titration method with detection in the range of 2 to 5 ppb. However, a number of compounds regularly present in water can interfere with detection. Colorimetric (spectrophotometric) and potentiometric (electrode-based) analyses are also available. Claudi and Mackie (1994) provide details and further references.

Adjuvant Use or Deactivation/Detoxification

Dilution is the most common means of detoxification of treated water.

The use of activated carbon filters allows removal of chlorine without replacement with another salt, and this is the most effective means of actual dechlorination (Menis-Croxall and deBruyn 1997).

Where chlorine dosage is at high concentrations or relatively frequent, dechlorination may be required to meet discharge regulations, unless outflow is to a storage lagoon or is diluted to acceptable levels. Dechlorination can be done by addition of sodium sulfite (Na_2SO_3), sodium bisulfite ($NaHSO_3$), sodium metabisulfite ($Na_2S_2O_5$), or sulfur dioxide (SO_2) (Barton 1993; Claudi and Mackie 1994). Sodium bisulfite in solution, known as liquid sulfite, is commonly used at 1.8 to 2.0 mg L^{-1} of sulfite per mg L^{-1} of residual chlorine, and can be fed into the discharge waters at any time as it acts rapidly (Claudi and Mackie 1994).

Application Techniques

Use of sodium hypochlorite solution. Apply at a single point where it will be able to be well-mixed into system water. Use accurate metering pumps or flowmeters engineered to handle the highly corrosive and alkaline properties of the solution. Diaphragm pumps are recommended, either motor or electric solenoid driven. Teflon fittings are required, and fiberglass piping is recommended; avoid stainless steel. Specific considerations for the holding tank, containment area, metering pump systems, and the skids to hold them are discussed by Menis-Croxall and deBruyn (1997). Use fiberglass piping for transporting concentrated solution to point of application.

Use of chlorine (Cl_2) gas. Injection of the gas is more hazardous due to the nature of the material.

Antidote Information

The following antidotes are from Materials Safety and Data Sheet for 5 percent sodium hypochlorite (ACROS Organics 1996):

a. *Eyes.* Flush eyes thoroughly with plenty of water for at least 15 minutes. Get medical aid immediately.

b. *Skin.* Flush with plenty of soap and water for at least 15 minutes while removing contaminated clothing and shoes. Get medical aid immediately.

c. *Ingestion.* Do not induce vomiting. Get medical aid immediately. Wash mouth out with water.

d. *Inhalation.* Get medical aid immediately. Remove the victim from exposure to fresh air immediately. If the victim is not breathing, give artificial respiration. If the victim's breathing is difficult, give oxygen.

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Chlorine Dioxide

Compared with chlorination with sodium hypochlorite, chlorine dioxide has several advantages. It is efficacious at lower concentrations; does not produce trihalomethanes (its by-products are sodium chloride and sodium chlorite); is not affected by pH or ammonia; and requires only short treatment duration and thus has less effect on system operations (Tsou et al. 1995). Some reports suggest that chlorine dioxide may be more effective than chlorine against adult mussels (Rusznak, Mincar, and Smolik 1994; Garrett and Laylor 1995; Matisoff, Brooks, and Bourland 1996). It has been used as a disinfectant for water for several decades. Disadvantages include the requirement for onsite generating equipment; storage of the component precursor chemicals (sodium hypochlorite and hypochloric acid); high oxidant demand, which may require higher treatment rates and reduce efficacy on the mussels; and conversion of the dioxide to chlorite, which limits the amount of ClO_2 that can be applied without excessive chlorite discharge.

Chemical Name and Formulations

Chlorine dioxide, ClO_2, is a yellow-green water-soluble gas. The generic chemical is available from numerous commercial sources.

Mode of Action

The gas is a biotoxic oxidant, causing membrane damage.

Application Strategies

Application is by injection of chlorine dioxide gas manufactured onsite using temporary or permanently installed generation and detoxification equipment. Chlorine dioxide has been applied in operational trials using a GENEROX™ generator from a ZEBRA MUSSEL BUSTER™ trailer (Holt and Ryan 1997).

Application can be on- or off-line.

Timing of Application

Application may be one of the following:

a. *Periodic*: approximately three times per year for 2 to 4 days at each time, to intake water. Can be used to perform periodic adult eradication (Tsou et al. 1995; Holt and Ryan 1997).

b. *Intermittent*: low-level feed of chlorine dioxide will control microbiological growth and prevent settlement of postveligers.

c. *Continuous or semicontinuous*: using permanently installed ClO_2 generation and detoxification equipment

Application Rates

The application may be at one of the following rates:

a. *Continuous*:

(1) Prevent veliger settlement: 0.125 mg L^{-1} ClO_2 (Klerks, Fraleigh, and Stevenson 1993).

(2) Veliger control: 0.25 to 5.0 mg L^{-1} for 3 to 9 days (Rusznak et al. 1995).

(3) Adult control: 0.15 to 5.0 mg L^{-1} above oxidant demand for 2 to 4 days (Smolik et al. 1995).

b. *Intermittent*: 0.25 mg L^{-1} for 15 minutes duration, four times daily, reduced settlement by 95 percent versus an untreated system and successfully controlled postveliger mean densities to less than 600 individuals per m^2 (Mallen et al. 1997).

c. *Periodic*: 2- to 4-day applications injected at 0.6 to 1 ppm, 3 to 4 times a year gave 70 to 100 percent mortality of adults in bioboxes (Tsou et al. 1995; Holt and Ryan 1997).

Maximum Water Concentration

Discharge limits depend on local, State, and Federal water restrictions as permitted under the National Pollutant Discharge Elimination System program.

Use Restrictions

Restrictions involve maximum contaminant levels on trihalomethanes, as well as on the sum of residual chlorine dioxide, chlorite, and chlorate (Van Benschoten et al. 1993).

Timing of Results

Considerable lag times between application and adult zebra mussel death have been observed, presumably due to shell closure when the presence of oxidant is sensed. Lag times of from 2 to 18 days are noted and generally decrease as chlorine concentration increases (Van Beschoten et al. 1993).

Resistance to chlorination can vary with age, size, and developmental stage of the mussel, with older and larger individuals being more resistant; veligers are much more susceptible than adults (Claudi and Mackie 1994).

Toxicological Data

For precursor sodium hypochlorite, see preceding section on hypochlorite.

Precautions

Chlorine dioxide has the following hazards and requires the following precautions:

a. Corrosive, severe respiratory and eye irritant.

b. May explosively decompose on shock, friction, concussion, or rapid heating.

c. Strong oxidant--reacts violently with combustible and reducing materials, and with mercury, ammonia, sulphur, and many organic compounds.

d. Safety glasses, face shield, gloves. Use effective ventilation.

e. In dilute solution, is explosive at concentrations over 10 percent.

Field Instructions and Guidance on Operational Applications

Wear splash-proof chemical goggles when working with liquid, unless full-face-piece respiratory protection is worn.

Wear dustproof goggles when there is a potential for exposure to the gas, unless full-face-piece respiratory protection is worn.

Adjuvant/Detoxicant/Deactivant Use

Residual chlorine has been neutralized with sodium bisulfite prior to discharge, at 7 ppm dechlorinating agent for 1 ppm oxidant (Tsou et al. 1995).

Application Techniques

Various mobile or onsite generation and application systems for sodium chlorite are available. These usually generate the gas from a combination of sodium hypochlorite, sodium chlorite, and hydrochloric acid.

The "vapor-phase" gaseous chlorine/liquid chlorite generation system is patented by Rio Linda (Rybarik, Byron, and Germer 1995).

The Drew CLO_2 generator reacts a sodium chlorite solution with sodium hypochlorite and hydrochloric acid (Tsou et al. 1995).

Once generated, the gaseous chloride dioxide is mixed with water and pumped to location of use.

Antidote Information

Use the following antidotes and first-aid procedures:

a. *Eyes*: Flush eyes thoroughly with plenty of water for at least 15 minutes. Get medical aid immediately.

b. *Skin*: Flush with plenty of soap and water for at least 15 minutes while removing contaminated clothing and shoes. Get medical aid immediately.

c. *Ingestion*: Do not induce vomiting. Get medical aid immediately. Wash mouth out with water.

d. *Inhalation*: Get medical aid immediately. Remove victim from exposure to fresh air immediately. If victim is not breathing, give artificial respiration. If victim's breathing is difficult, give oxygen.

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3 Nonchlorine Oxidizing Chemicals

In addition to the chlorinating chemicals, the oxidizers bromine and potassium permanganate can be used for treatment of zebra mussels.

Bromine

Bromine is an oxidizing chemical that is used for antifouling purposes in such forms as activated bromine, sodium bromide, bromine chloride, and mixtures of bromine and chlorine or other chemicals (Claudi and Mackie 1994), and it is approved for use in the United States for zebra mussel control. It is more effective as an oxidizing agent when water pH is above 8.0 (Fellers, Flock, and Conley 1988). Bromine is also used as a chlorine enhancer designed to minimize the amount of chlorine required to prevent macrofouling, and the proprietary ACTI-BROM® compounds are used in this way. BROMICIDE® and LIQUIBROM™ are other examples of bromine, marketed by Great Lakes Chemical Corporation, West Lafayette, IN.

In the past it was suggested that bromine was less toxic than chlorine to nontarget species, but this has been shown not to be the case (Howe et al. 1994). Total amount of oxidant required for mussel control is approximately the same as chlorine (Claudi and Mackie 1994).

ACTI-BROM

ACTI-BROM® is a chlorine enhancer system that consists of an aqueous solution containing a bromide salt and an oxyalkylate biodispersant (surfactant) designed to improve chlorine activity. The ACTI-BROM technology was originally patented for control of the Asiatic clam and barnacles, and the application program has been found to be effective on zebra mussels (McCarthy and Trulear 1992). It can be particularly useful in situations where control cannot be obtained within the legal chlorination limits or where sodium hypochlorite is being considered as a gaseous chlorine alternative. This compound can be used in either eradication or prevention treatment programs.

Chemical Name and Commercial Formulations

This molluscicide is characterized as follows:

a. Chemical name: Sodium bromide, $NaBr_2$.

b. Formulation: ACTI-BROM 1338 Biodispersant.

- 42.8 percent sodium bromide plus oxyalkylate.
- Aqueous solution.

c. Source: Nalco Chemical Company
One Nalco Center
Naperville, IL 60563-1198
(630) 305-1000
Emergencies: 1-800-462-5378

Mode of Action

ACTI-BROM is an oxidizing biocide program that utilizes a chlorine source, either gas or sodium hypochlorite, to activate a bromide/biodispersant chemistry. On their own, the bromide salt and biodispersant present in ACTI-BROM are nonmolluscicidal; however, in the presence of chlorine gas or sodium hypochlorite in situ, ACTI-BROM's bromine portion is activated to form hypobromous acid and hypobromite ion, depending on water pH (McCarthy and Trulear 1992). Both these forms of bromine are lethal to zebra mussels, destroying vital tissue. Hypochlorous acids are also formed, and the ratio of hypobromous to hypochlorous acid can be varied by altering the molar ratios between sodium bromide-surfactant and the chlorine source.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

or

$$NaOCl + H_2O \rightarrow HOCl + NaOH$$

then

$$HOCl + NaBr \rightarrow HOBr + NaCl$$

The oxyalkylate surfactant, present at 5 to 10 ppb, is not expected to contribute to toxicity, but may inhibit settling and attachment by acting as a biodispersant.

Application Strategies

Add sufficient ACTI-BROM and oxidize with either chlorine gas or sodium hypochlorite solution to achieve residual bromine levels as needed.

Two primary types of treatment programs are recommended for controlling zebra mussels with this product:

a. Eradication: eliminate accumulated mussels.

b. Preventive: prevent migration and attachment of zebra mussels in a system.

Timing of Application

Application is timed according to the following treatments:

a. Periodic: usually applied twice per year.

b. Eradication: apply one to three times per year during warm season: immediately after the annual peak in reproduction (typically in June or July), and at the end of the season (October or November) (Nalco Chemical Company 1996).

c. Preventive: treat throughout warm weather season. Can be added whenever chlorination is applied.

Application Rates

Add sufficient ACTI-BROM 1338 and oxidize with either gas chlorine or sodium hypochlorite solution to achieve a reisdual bromine level of 0.5 to 5 ppm or as needed to maintain control of the system.

Periodically apply on a continuous basis for 1 to 3 weeks at 0.1 to 0.5 ppm free residual oxidant to eradicate juvenile and adult mussels (McCarthy and Trulear 1992). This concentration is based on a bromine to chlorine ratio (molar basis) of 1:1.

Treatment of adults with a total residual oxidant level of 0.1 ppm indicated that 18-day continuous contact gave up to 60 percent mortality, and 30-day contact 90 to 100 percent mortality (Sawyko 1994).

Maximum Water Concentration

This product is registered as a pesticide by the U.S. Environmental Protection Agency and must be handled and fed within the limits of the label instructions.

Use Restrictions

Use with a registered gaseous chlorine or sodium hypochlorite product.

Apply in accordance with the label and with the site National Pollutant Discharge Elimination System permit.

For zebra mussel control in New York State, the Department of Environmental Conservation provides a “generic modification” for holders of State Pollutant Discharge Elimination System permits to allow bromine treatments, including ACTI-BROM.

Timing and Appearance of Effects

Effect is synchronous with chlorine cotreatment effect. It produces more rapid effects in veliger stages than in adults.

Toxicological Data

The Signal Word is Caution.

Toxicological data for bromine to aquatic species is shown in the following tabulation:

Aquatic Toxicology Data for Various Forms of Bromine[1]

Organism	Test	Data[2]
	ACTI-BROM	
Rainbow trout	96-hr Static	LC_{50} > 1,000 mg/L NOEL 1,000 ppm
Bluegill sunfish	96-hr Static	LC_{50} > 1,000 mg/L NOEL 1,000 ppm
	Sodium Bromide	
Fathead minnow	96-hr Static	LC_{50} 16,479 mg/L
Poecilia reticulata	96-hr Static	LC_{50} 225 mg/L
Daphnia magna	48-hr Static	LC_{50} 7,900 mg/L
	Hypobromous Acid (from Product)	
Fathead minnow	96-hr Flow-through	LC_{50} 0.079 mg/L (as Br_2)
Daphnia magna	48-hr Flow-through	LC_{50} 0.038 mg/L (as Br_2)
	Hypobromous Acid (from Sodium Bromide)	
Bluegill sunfish	96-hr Static	LC_{50} 0.52 mg/L (as Br_2) NOEC 0.30 ppm (as Br_2)
Rainbow trout	96-hr Static	LC_{50} 0.23 mg/L (as Br_2)
Fathead minnow	96-hr Flow-through	LC_{50} 0.097 mg/L (as Br_2)
Sheepshead minnow	96-hr Flow-through	LC_{50} 0.19 mg/L (as Br_2) NOEC 0.08 ppm
Daphnia magna	48-hr Static 48-hr Flow-through	LC_{50} 0.71 mg/L (as Br_2) NOEC 0.41 ppm LC_{50} 0.038 mg/L (as Br_2)
Eastern oysters	96-hr Flow-through	EC_{50} 0.54 mg/L (as Br_2)
Mysid shrimp	96-hr Flow-through	LC_{50} 0.54 mg/L (as Br_2)

[1] From Materials Safety and Data Sheet (Nalco Chemical Company 1992); see also Electric Power Research Institute (1993).
[2] LC_{50} = Median lethal concentration
NOEL = No-observed-effect level
NOEC = No-observed-effect concentration

Precautions

ACTI-BROM is harmful if swallowed and causes moderate eye irritation. Do not get in eyes, on skin, or on clothing.

Field Instructions and Guidance on Operational Applications

Use impermeable gloves and chemical splash goggles when handling.

Although ACTI-BROM produced mortality below 20 °C (68 °F), lower water temperatures may reduce the effectiveness of treatment (Sawyko 1994).

Monitoring kits for use in checking zebra mussel veliger density and settling in a water system and experimental systems for determining adult mussel mortality under local water quality conditions are available from Nalco.

Adjuvant and Deactivation Use

Use ACTI-BROM as an adjuvant to chlorination treatment.

A 60 percent potassium hypochlorite (solid) is used for weekly addition to supplement bromine treatment (Schnelle and Strimple 1995).

It may be necessary to use a dehalogenating material such as a sodium bisulfite to reduce halogen levels prior to discharge, depending on outfall permits.

Application Techniques

ACTI-BROM can be added whenever chlorination is applied. It can be fed with two pumps, one for sodium hypochlorite and one for sodium bromide solution, directly from the drum or bulk storage tank to a location in the chlorination system where it will be uniformly mixed and thoroughly distributed.

Feed as far upstream as possible.

Monitor treatment levels of ACTI-BROM and oxidant with test kits for bromine or chlorine.

Antidote Information

Use the following antidote and first aid procedures:

a. *Eyes*: flush with water for 15 minutes. Call a physician.

b. *Skin*: wash thoroughly with soap and rinse with water. Call a physician.

c. *Ingestion*: induce vomiting and give water, except when the victim is unconscious, having trouble breathing, or in convulsions. Call a physician.

d. Inhalation: remove victim to fresh air. Treat symptoms. Call a physician.

e. Emergencies: 1-800-462-5378 (Nalco, 24 hour-a-day response).

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Potassium Permanganate

Potassium permanganate, a purplish chemical whose use as a disinfectant was originally developed in the 1800's, is a strong nonchlorine oxidant with a long history of safe use in drinking water, wastewater, and chemical manufacturing industries. It has been used by water treatment plants as an oxidizer since the turn of the century, and is commonly used in municipal facilities for water purification. It is widely used for oxidation of iron and manganese and to correct taste and odor problems in treated water because of its ability to produce oxidation reactions with inorganic compounds and organic substances (Claudi and Mackie 1994).

Potassium permanganate produces effective control of adult zebra mussel at 2.0 mg L^{-1}, and inhibits veliger settlement at 1.0 mg L^{-1} and below (San Giacomo and Wymer 1997). It does not produce trihalomethanes or haloacetic acids (San Giacomo and Wymer 1997). Although it costs more than chlorine, it can be less expensive than proprietary molluscicide chemicals. It requires a long contact time. It may not be 100 percent effective (Fraleigh et al. 1993). Overdosing may result in an unacceptable pink coloration in water. Agencies using this control method include the City of Baltimore, Public Works (Balog et al. 1995) and the City of Buffalo, NY (San Giacomo and Wymer 1997).

CAIROX ZM®

Information on CAIROX ZM® Free-Flowing Grade Potassium Permanganate, a proprietary potassium permanganate compound that is also registered for control of zebra mussels, is provided as an example of the use of this chemical. CAIROX ZM is effective in the control of zebra mussels, biofilm, and other biofoulants such as plankton, algae, and microorganisms in raw water intake lines of drinking water and industrial water treatment systems.

Chemical Name and Formulations

a. *Chemical name*: Potassium permanganate, $KMnO_4$

b. *Formulation*: CAIROX ZM Free-Flowing Grade Potassium Permanganate

- Potassium permanganate 97 percent
- Granular
- Meets American Water Works Association Standard B 603 (1993).

c. *Source*: Carus Chemical Company, Carus Corporation
315 Fifth Street
P.O. Box 599
Peru, IL 61354-0599
(815) 223-1500

d. EPA Registration No.: 8429-9

Mode of Action

MnO_4^- is not the thermodynamically stable form of manganese in water; thus, permanganate tends to oxidize very slowly in water with the evolution of oxygen:

$$4\ MnO_4^- + 4\ H^+\ \text{®}\ 4\ MnO_2 + 2\ H_2O + O_2$$

Potassium permanganate has oxidizing activity. It has been observed that adult mussels retract their siphons while potassium permanganate is passing through water.

Application Strategies

Use this compound on-line in continuous dosage to eliminate mussels.

Add CAIROX ZM to raw water intake lines as early in the treatment system as possible.

It can be combined with chlorine.

Timing of Application

Apply this compound during summer mussel season, especially during the veliger settling phase.

Application Rates

Concentrations of CAIROX ZM required for oxidation of contaminants, typically up to 5 mg L^{-1}, are sufficient for the control of zebra mussels and other biofoulants.

Monitor to maintain a low residual concentration of less than 1 mg L^{-1} at the point of entry into a treatment plant.

Actual solubility in local water and effective doses should be determined using laboratory jar tests (Carus 1997).

Klerks, Fraleigh, and Stevenson (1993) showed that static exposure of 2.5 mg L^{-1} potassium permanganate resulted in 27 percent mortality of veligers, while in flow-through exposures veligers decreased by 90 percent with this concentration.

Balog et al. (1995) reported plans for the use of intermittent treatments at 0.35 mg L^{-1} residual level for at least 30 min in the treatment area for a municipal water treatment plant.

CAIROX ZM can be followed by chlorine.

Maximum Water Concentration

American National Standards Institute/National Sanitation Foundation Standard 60-1997 (1997) gives maximum use level as 50 mg L^{-1}.

Ensure that residues of manganese in finished potable water are limited to no more than 0.05 mg L^{-1}.

Use Restrictions

Ensure that residues of manganese in finished potable water are limited to no more than 0.05 mg L^{-1}.

A filtration plant residual of less than 0.25 mg L^{-1} (ppm) is needed to prevent pink discoloration of drinking water.

Do not use in facilities discharging directly or indirectly to estuarine or marine environments. Do not discharge effluent containing this product into lakes, streams, ponds, or public waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Timing of Results

Treatment effects on individuals occur within a few days. Continue treatment to system to maintain efficacy.

Toxicological Data

The Signal Word is Danger.

Toxicology of potassium permanganate to aquatic species is listed in the accompanying tabulation.

Precautions

Take the following precautions with this compound:

a. Strong oxidizer; keep from contact with combustible materials.

b. Corrosive; causes eye and skin damage. Avoid contact with eyes, skin, mucous membranes.

Aquatic Toxicity of Potassium Permanganate		
Organism	**Test/Water Condition**	**Level, mg L^{-1}**
Rainbow trout	96-hr LC_{50} 12 ºC 160-180 mg L^{-1} $CaCO_3$ pH 8.1	1.72
Channel catfish	96-hr LC_{50} 12 ºC 160-180 mg L^{-1} $CaCO_3$ pH 7.8	1.00
Rainbow trout	96-hr LC_{50} 12 ºC soft water pH 7.5	1.80
Channel catfish	96-hr LC_{50} 12 ºC soft water pH 7.5	0.75
Note: from Marking and Bills 1975.		

c. Prolonged inhalation of manganese compounds above the permissible exposure limit may cause lung irritation and central nervous system disorders.

d. When handling, use safety goggles, rubber gloves, and respirators. Avoid breathing dust.

e. Do not take internally; harmful if swallowed.

f. Toxic to birds and aquatic invertebrates.

Field Instructions and Guidance on Operational Applications

CAIROX is available in 25-kg pails, 50-kg kegs, 150-kg drums, 1,500-kg cycle-bins, and bulk up to 21,772 kg (48,000 lb).

Under normal conditions, CAIROX is stable. It will keep indefinitely if stored in a cool, dry area in a closed container. Avoid contact with acids, peroxides, and all combustible organic or readily oxidizable materials including metal powders. With hydrochloric acid, chlorine gas is liberated. It may decompose if exposed to heat. Store at less than 302 ºF (150 ºC).

Where exposure to airborne CAIROX may exist, a user should wear goggles, rubber or plastic gloves, and an approved National Institute for Occupational Safety and Health/Mine Safety and Health Administration dust and mist respirator. Normal clothing that covers arms and legs and a rubber or plastic apron are suitable attire. Always provide ventilation in the work area.

Following exposure to CAIROX potassium permanganate, brown stains of manganese dioxide often form on the skin as a natural decomposition product. These stains are harmless and can be removed using a solution composed of 3 parts 3 percent hydrogen peroxide, 4 parts 5 percent food grade white vinegar, and 3 parts tap water. Wash off excess when the stain is gone. Do not use if skin becomes red or irritated, or on sensitive tissue such as eyes, mucous membranes, open wounds, or burns.

Adjuvant/Detoxicant/Deactivant Use

None is specified.

Application Techniques

Dry flowable product can be poured from pails or handled in bulk.

Antidote Information

Use the following antidotes:

a. *If exposed to this product*: flood eyes with water for at least 15 minutes; wash skin thoroughly with soap and water; remove clothing for washing.

b. *If swallowed*: if the victim is conscious, give one or two glasses of water. Never give anything by mouth to an unconscious or convulsing person.

c. *If in eyes*: flood eyes with water for at least 15 minutes, holding the lids open. Do not attempt to use chemical antidotes.

d. *If on skin*: wash thoroughly with soap and water.

e. *If inhaled*: remove victim to fresh air.

f. *Emergency telephone*: 1-800-435-6856
CHEMTREC: 1-800-424-9300

References

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4 Nonoxidizing Molluscicides

This group of chemicals includes most of the congeneric and commercial formulations that have been recently registered specifically for use in zebra mussel control. Their chemistry and activity differ from the oxidizing compounds, and they provide a different range of potential applications.

Quaternary and Polyquaternary Ammonium Compounds

These organic compounds comprise chemicals known as quaternary ammonium compounds (QAC=s) and polyquaternary ammonium compounds (poly-QACs, or polyquats).

BULAB 6002

BULAB® 6002 is a liquid cationic polyquaternary ammonium compound, a straight-chain ionene polymer with positively charged nitrogen atoms in the backbone of its polymeric chain (McMahon, Shipman, and Long 1993). It is used for algae control in swimming pools and as a microbicide for the control of microorganisms in commercial and industrial water systems. It also is an effective molluscicide and can prevent biofouling by mollusks (McMahon and Lutey 1988; McMahon, Shipman, and Ollech 1989; Waller et al. 1993; Buckmann Laboratories, Inc., 1998). It is effective with or without the use of chlorine. It is approved for use in drinking water by the American National Standards Institute/National Sanitation Foundation (ANSI/NSF 1997).

Chemical Name and Commercial Formulations

This compound has the following characteristics:

a. Chemical name:

- poly[oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylene dichloride
- $C_{10}H_{24}N_2OCl_2$
- Also known as PQ1 or WSCP

b. Formulation: BULAB 6002

- 60 percent polymeric quaternary ammonium
- Water-soluble liquid; U.S. Environmental Protection Agency Reg. No. 1448-42

c. Source: Buckman Laboratories, Inc.
1256 McLean Boulevard
Memphis, TN 38108
(901) 278-0330
1-800-BUCKMAN

Mode of Action

As a poly-QAC, BULAB 6002 binds to negatively charged surfaces including those of microorganisms and mollusk membranes. It is not detected by mussels as a noxious compound and closure response is not provoked; kill can occur quickly.

Application Strategies

The compound can be applied as short-term, continuous, or intermittent treatments.

Timing of Application

The compound is generally used for one-time application, end of season, or periodic use.

Application Rates

To control mollusks in recirculating or once-through cooling water and industrial systems using continuous or intermittent application, add BULAB 6002 at dosage rates of 0.2 to 2.2 fluid ounces of BULAB 6002 per 1,000 gallons of water (15.6 ml to 172 ml to 10,000 L), or 2 to 20 ppm product. Addition should be made continuously or intermittently to the intake water. Continuous addition is required for noticeably fouled systems.

Intermittent feeding is used to maintain control.

Mollusk fouling has been prevented by concentrations as low as 2 ppm.

Initial concentrations of 2 to 5 mg L^{-1} can be used up to 21 days. The long-term limit is 0.5 mg L^{-1}.

The following tabulation summarizes laboratory studies showing efficacies of this product and the relationship of exposure time to concentration. Martin, Mackie, and Baker (1993a) showed that toxicity was temperature dependent.

Activity of BULAB 6002 on Zebra Mussel						
Concentration mg L^{-1}	LT_{50}, hr		LT_{100}, hr		MTD, hr	
	MMB	MSL	MMB	MSL	MMB	MSL
1.0	168	499	250	680	514	175
2.0	148	216	250	313	231	166
4.0	108	174	196	244	189	123
8.0	96	124	144	197	147	107

Note: MMB = Martin. Mackie, and Baker (1993b).
MSL = McMahon, Shipman, and Long (1993).
LT_{50}, LT_{100} = time to percent mortality.
MTD = mean time to death.

Maximum Water Concentration

The long-term limit in potable water is 0.5 mg L^{-1} (ppm) maximum.

Use Restrictions

Initial concentrations of 2 to 5 mg L^{-1} can be used up to 21 days. The long-term limit is 0.5 mg L^{-1} in water.

This product is toxic to fish and aquatic organisms at certain concentrations. Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance, contact the governing State Water Board or Regional Office of the U.S. Environmental Protection Agency.

It is approved for potable water systems for mollusk treatment at 0.5 ppm maximum (ANSI/NSF 1997).

Use in closed systems is unrestricted.

Timing and Appearance of Effects

Lethality is seen within 5 days, depending on concentration. Continue applications as recommended for full treatment effect.

Toxicological Data

The following tabulation lists the toxicity of BULAB 6002:

Toxicity of Active Product, BULAB 6002		
Organism	**Test, LC_{50}**	**Limit, mg L^{-1}**
Daphnia magna	48-hr	0.37
Bluegill sunfish	96-hr	0.21
Rainbow trout	96-hr	0.047
Fathead minnow	96-hr	0.26
Sheepshead minnow	96-hr	> 600
Mysid shrimp	96-hr	13.0
Quahog clam	96-hr	0.35
Note: From Buckman Laboratories, Inc., 1997.		

BULAB 6002 does not degrade readily in water but adsorbs strongly to sediments, clay particles, organic matter and other negatively charged surfaces, so that water column concentrations are normally very low: adsorption and biodegradation are probably the dominant fate processes in aquatic systems (Electric Power Research Institute 1993).

Precautions

This compound is harmful if swallowed. Avoid breathing vapors. Avoid contact with skin, eyes, or clothing.

It is a mild irritant to eyes, nonirritating to skin, and may cause irritation or corrosion of mucous membranes and lungs.

Rubber gloves, indirect ventilation goggles, body-protective clothing, and rubber safety shoes are required.

Field Instructions and Guidance on Operational Applications

See Buckman Laboratories, Inc. (1997), for extensive list of construction materials satisfactory for use in handling BULAB 6002.

Adjuvant Use

There is no adjuvant use. It can be applied with or without chlorine.

Application Techniques

Apply to intake water, at a point of maximum water agitation.

Antidote Information

Use the following antidotes:

a. If swallowed: do not induce vomiting. Rinse with copious amounts of water or milk. Irrigate the esophagus and dilute the stomach content by slowly giving one to two glasses of water or milk. If person is comatose or convulsing, do not give fluids by mouth. Get medical assistance immediately; take individual to nearest medical facility.

b. If in eyes: rinse eyes immediately for at least 15 minutes with copious amounts of water. Seek medical attention.

c. If on skin: rinse with large amounts of water and wash with soap and water. Remove contaminated clothing and wash before reuse. If irritation occurs, seek medical attention.

d. If inhaled: move person to a well-ventilated place and apply artificial respiration if required. Call a physician.

e. Emergency phone number, 24 hour: (901) 767-2722.

References

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Calgon H-130M

This compound is a nonoxidizing liquid organic compound containing a solution of polyquaternary alkyl ammonium registered for use as a molluscicide in industrial once-through freshwater cooling water systems. Calgon H-130M controls zebra mussel and the Asiatic clam in veliger, juvenile, and adult forms. Because of its need for proper deactivation prior to discharge, it is sold only as part of a complete Calgon mollusk treatment application service, and is to be used only with supervision from a Calgon representative.

Chemical Name and Commercial Formulations

This compound has the following characteristics:

a. Chemical Name: Didecyldimethylammonium chloride, known as DDMAC.

b. Formulation: H-130M; 50 percent DDMAC; liquid, U.S. Environmental Protection Agency Registration No. 6836-203-10445.

c. Source: Calgon Corporation
P.O. Box 1346
Pittsburgh, PA 15230-1346
(412) 777-8000
Health and Environmental Affairs: (412) 494-8000

Mode of Action

Antifouling activity results from coating, surfactant action.

Application Strategies

Slug feed for once-through systems.

Timing of Application

Apply up to four times per year as periodic treatment to limit accumulation of adults.

Application Rates

Apply 1 to 10 ml H-130M per 1,000 L (1-10 ppm) water (0.15 to 1.5 fluid ounces per 1,000 gal of water) to give 1 to 10 mg L^{-1} (ppm) (Calgon Corporation 1996a).

Treatment is typically a 24-hr feed period at 1.5 ppm to the inlet of the plant to maintain a residual at the discharge of 0.5 ppm. Actual treatment durations may vary from site to site dependent on water temperature and other site-specific conditions.

Do not apply H-130M more than four times per year. The duration of the treatment must not exceed 120 hr per application.

Refer to the following tabulation for efficacy data.

Toxicity of Active Ingredient (DDMAC) to Target Organisms

Organism/Size	Median Lethal Concentration	
	48-hr Test mg L^{-1}	48-hr Post Exposure mg L^{-1}
Zebra mussel, 20- to 25-mm diameter	0.85	0.38
Zebra mussel, 5- to 8-mm diameter	1.12	0.59
Threehorn wartyback	6.12	3.72

Note: from Waller et al. 1993; Fisher et al. 1994.

Maximum Water Concentration

H-130M must be deactivated prior to discharge.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, ocean or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit and notification of the permitting authority in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Use Restrictions

H-130M is toxic to fish.

This compound requires proper deactivation prior to discharge.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, ocean or other waters unless in accordance with the requirements of an NPDES permit and notification of the permitting authority in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Do not apply H-130M more than four times per year. The duration of the treatment must not exceed 120 hr per application.

Use of this product in either public/municipal or single- or multiple-family private/residential potable/drinking water systems is strictly prohibited. Use of this product in any cooling water system that discharges effluent within 1/4 mile of either a public/municipal or single- or multiple-family private/residential potable/drinking water intake is strictly prohibited.

Do not use water containing residues from use of this product to irrigate crops used for food or feed.

Do not contaminate water, food, or feed by storage or disposal.

Timing and Appearance of Effects

Mussels are affected within 2 days of application (see preceding tabulation).

Toxicological Data

The Signal Word is Danger

The following tabulation describes the aquatic toxicity of this compound.

Toxicity of Active Ingredient (DDMAC) of H-130M

Organism	Test	Median Lethal Concentration of H-130M, mg L^{-1}
Rainbow trout	96-hr	1.1
Coho salmon	96-hr	1.0
Daphnia magna	48-hr	0.094
Mysid shrimp	96-hr	0.069
Bluegill sunfish	96-hr	0.32 - 0.59
Note: from Calgon Corporation 1996b		

Precautions

This compound is corrosive and harmful or fatal if swallowed. Do not get in eyes or on skin or clothing. It can cause severe damage to eyes and skin. Wear safety glasses, goggles, or face shield and rubber gloves when handling. Avoid breathing spray mist.

H-130M is a flammable/combustible liquid and vapor. Do not use, pour, spill, or store near heat or open flame.

Do not use or compound H-130M with any reducing or oxidizing agents (such as calcium hypochlorite, solid perchlorate, or nitric acid) since such mixtures may be explosive. Do not use in conjunction with soap or any anionic wetting agent.

Field Instructions and Guidance on Operational Applications

Rate of adsorption onto target mollusks is temperature dependent.

H-130M residual is monitored throughout the plant system and prior to discharge using a test procedure sensitive down to 20 ppb. A composite water sample is sent to an outside laboratory, and test results are provided to the customer to verify that effluent water is safe.

Recommended handling materials for pump and piping are polypropylene, polyethylene, Hypalon, stainless steel, epoxy phenolic-lined steel, or isophthalic polyester resins.

Adjuvant/Detoxicant/Deactivant Use

The compound must be deactivated prior to discharge from the system using bentonite clay at a minimum ratio of 5 ppm clay to 1 ppm product.

The proprietary product CA-35 is also used to deactivate H-130M in plant water prior to discharge to the environment. The feed rate of the CA-35 is typically 5 ppm for every 1 ppm of H-130M fed to the inlet water. CA-35 feed continues at least 2 hr past the time when the H-130M is discontinued, to assure complete deactivation of biocide remaining in the system.

Application Techniques

H-130M is fed as close to the raw water inlet as possible without risking the release of the chemical into the environment.

H-130M should be fed as received if the product is fed directly from drum or pail. If the product is slug-fed by hand, prepare a 2:1 mixture of water to biocide. Prepare mixture by slowly adding product to the mix water. This procedure minimizes foaming during dilution and when feeding the diluted product to water. Apply at a point in the system where the product will be uniformly mixed.

Antidote Information

In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. In case of contact with eyes, call a physician immediately.

If the compound is swallowed, immediately drink 3 to 4 glasses of milk, or egg whites, or gelatin solution; if these are not available, drink a large quantity of water. Call a physician immediately.

Note to physician: probable mucosal damage may contraindicate use of gastric lavage. Measures against circulatory shock, respiratory depression, and convulsion may be needed.

References

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Clam-Trol J

The primary active ingredients of these products are cationic surfactants of the n-alkyldimethyl-benzyl ammonium chloride (ADBAC) family. These quaternary ammonium compounds have various length carbon chains and are short-lived in plant systems and the environment because of rapid absorption onto anionic substrates and sediments in natural aquatic ecosystems. They are used for cooling and service water systems.

Chemical Name and Commercial Formulations

The active ingredients of these products have the following chemical names:

a. ADBAC,Quat n-Alkyl (C12, C14, and C16) dimethylbenzyl ammonium chloride

b. DGH: Dodecylguanidine hydrochloride

Their formulations are as follows:

a. Clam-Trol CT-1:

- 8 percent n-alkyl (C12-40 percent, C14-50 percent, C16-10 percent) dimethylbenzyl ammonium chloride
- 5 percent dodecylguanidine hydrochloride
- Liquid
- U.S. Environmental Protection Agency Registration No. 3876-145

b. Clam-Trol CT-2:

- 50 percent n-alkyl (C12-50 percent, C14-40 percent, and C16-10 percent) dimethylbenzyl ammonium chloride
- Liquid

c. Clam-Trol CT-4

- 10 percent n-alkyl (C12-50 percent, C14-40 percent, and C16-10 percent) dimethylbenzyl ammonium chloride
- Liquid

d. Source BetzDearborn, Inc.
4636 Somerton Road
Trevose, PA 19053
Information: (215) 355-3300
Emergency: 1-800-877-1940

Mode of Action

These products work by adsorbence to system components. Mussels do not detect them as noxious compounds and they do not close their shells. This allows them to be affected and killed quickly, with significant mortality in 4 to 24 hr.

Clam-Trol causes detachment of adults and is effective on mollusks at all life stages. It also controls microfouling organisms.

The formulations have the following effects:

a. *CT-1*: For control of mollusca, barnacles, hydrozoa, bryozoa, bacteria, fungi, and algae. Effective on zebra mussels, Asiatic clams, ribbed mussels, blue mussels, and most other freshwater and saltwater mollusks. Also controls bacterial, fungal, and algal slime.

b. *CT-2*: Effective on freshwater and saltwater mollusks, including zebra mussels, Asiatic clams, ribbed mussels, blue mussels, and oysters. Assists in controlling microbial growth including algae, bacteria, and fungi.

c. *CT-4*: Effective on zebra mussels and Asiatic clams.

Application Strategies

Apply these compounds as follows:

a. Continuous, intermittent, or as needed. Frequency of feeding and duration of treatment depend upon severity of problem.

b. Periodic, short-term (6 to 24 hr) applications to water on a proactive basis to prevent mollusks from growing to a fouling size.

c. Intermittent or slug method: when system is noticeably fouled, apply initial dose to achieve control. Repeat the process periodically to inhibit recolonization by larvae (veligers) and juvenile clams and mussels.

d. Applications may be able to be conducted off-line or at reduced flow.

e. Registered use areas in which to control mollusks with these products are as follows:

(1) CT-1: recirculating and once-through cooling systems, influent cooling systems, auxiliary water and wastewater systems, fire protection systems, intake pump bays and intake screen area, storage tanks and associated piping, settling ponds or lagoons, transport spillways or canals.

(2) CT-2: recirculating and once-through cooling systems, service water, auxiliary water, influent, fire protection, and wastewater systems. For auxiliary water/service water and wastewater systems,

may be added to the system water or by spraying onto a waste pile as needed.

(3) CT-3: cooling towers and once-through freshwater cooling systems.

(4) CT-4: once-through freshwater cooling systems.

Sensitivity of various life stages has been studied by Waller et al. (1993) and Fisher et al. (1994).

Timing of Application

They may be applied continuously, intermittently, or as needed during the season of activity.

Application Rates

Rates vary by product formulation and system. See accompanying tabulations (BetzDearborn, Inc., 1988, 1993a, 1993b). Badly fouled systems must be cleaned before treatment is begun.

Clam-Trol CT-1 is applied as follows:

a. Warmer water temperatures and longer contact times reduce the concentration of CT-1 needed for effective kills.

b. Product weight is 1 kg L^{-1} (8.5 lb/gal), and concentrations are based on product.

c. Apply as follows for recirculating cooling water systems:

(1) Intermittent or slug method: Initially when fouled, 360 g to 2.4 kg per 10,000 L water (0.3 to 2.0 lb per 1,000 gal of water), 36 to 240 ppm. Repeat until control is achieved. Subsequently, apply 180 g to 1.8 kg per 10,000 L water (0.15 to 1.5 lb per 1,000 gal of water), 18 to 180 ppm, every 3 days, or as needed to maintain control.

(2) Continuous feed method: Initially when fouled, 360 g to 2.4 kg per 10,000 L water (0.3 to 2.0 lb per 1,000 gal of water), 36 to 240 ppm. Subsequently, maintain 60 to 600 g per 10,000 L water (0.05 to 0.5 lb per 1,000 gal water), 6 to 60 ppm, in system.

d. Apply as follows for once-through industrial cooling water systems:

(1) Intermittent or slug method: Initially when fouled, 240 g to 1.2 kg per 10,000 L water (0.2 to 1.0 lb per 1,000 gal of water), 24 to 120 ppm, at minimum treatment intervals of 15 min. Repeat until control is achieved. Subsequently, 60 to 600 g per 10,000 L water

Application Methods for Clam-Trol Formulations

Product/System	Intermittent or Slug	Continuous Feed	Other
CT-1			
Recirculating cooling water	Initial: 0.3 - 2.0 lb/1,000 gal 360 g - 2.4 kg/10,000 L (36 - 240 ppm) Subsequent: 0.15 - 1.5 lb/1,000 gal 180 - 1.8 kg/10,000 L (18 - 180 ppm) Every 3 days/as needed	Initial: 0.3 - 2.0 lb/1,000 gal 360 g - 2.4 kg/10,000 L (36 - 240 ppm) Subsequent: 0.05 - 0.5 lb/1,000 gal 60 - 600 g/10,000 L (6 - 60 ppm)	
Once-through industrial cooling water	Initial: 0.2 - 1.0 lb/1,000 gal 240 g - 1.2 kg/10,000 L (24 - 120 ppm) Subsequent: 0.05 - 0.5 lb/1,000 gal 60 - 600 g/10,000 L (6 - 60 ppm) As needed	Initial: 0.2 - 1.0 lb/1,000 gal 240 g - 1.2 kg/10,000 L (24 - 120 ppm) Subsequent: 0.02 - 0.2 lb/1,000 gal 24 - 240 g/10,000 L (2.4 - 24 ppm)	
Auxiliary water/wastewater	Initial: 1.5 - 4 lb/1000 gal 1.8 - 4.8 kg/10,000 L for 4 to 8 hr 1 to 4 times/week (180 - 480 ppm) Subsequent: 0.75 - 2 lb/1000 gal 900 g - 2.4 kg/10,000 L (90 - 240 ppm)		Spray onto waste pile
CT-2			
Recirculating or once-through Industrial/commercial cooling water systems	Initial: 0.016 - 0.166 lb/1,000 gal 20 - 200 g/10,000 L (2 - 20 ppm) Maintain 3 - 48 hr		
Auxiliary water/service water and wastewater systems	0.3 to 1.3 lb/1,000 gal 360 g - 1.56 kg/10,000 L (36 - 156 ppm) for 4 - 8 hr 1 - 4 x/week Subsequent: 0.15 - 0.65 lb/1,000 gal 180 - 780 g/10,000 L 18 to 78 ppm		Spray onto waste pile
CT-4			
Once-through freshwater cooling systems	1.28 - 12.8 fl oz/1,000 gal 100 ml - 1 L/10,000 L 1 - 10 ppm ai Treat #120 hr # 4 times per year		

Application Rates of Clam-Trol Formulations for Various Water-Handling Systems

Water/System Application Method	Clam-Trol Product		
	CT-1	CT-2	CT-4
Recirculating Cooling Water			
Intermittent or slug	Initial: 0.3 - 2.0 lb/1,000 gal 360 g - 2.4 kg/10,000 L (36 - 240 ppm) Subsequent: 0.15 - 1.5 lb/1,000 gal 180 - 1.8 kg/10,000 L (18 - 180 ppm) Every 3 days/as needed	Initial: 0.016 - 0.166 lb/1,000 gal 20 - 200 g/10,000 L (2 - 20 ppm) Maintain 3 - 48 hr	
Continuous feed:	Initial: 0.3 -2.0 lb/1,000 gal 360 g - 2.4 kg/10,000 L (36 - 240 ppm) Subsequent: 0.05 - 0.5 lb/1,000 gal 60 - 600 g/10,000 L (6 - 60 ppm)		
Once-Through Freshwater Cooling			
Intermittent or slug	Initial: 0.2 - 1.0 lb/1,000 gal 240 g - 1.2 kg/10,000 L (24 - 120 ppm) Subsequent: 0.05 - 0.5 lb/1,000 gal 60 - 600 g/10,000 L (6 - 60 ppm) As needed	Initial: 0.016 - 0.166 lb/1,000 gal 20 - 200 g/10,000 L (2 - 20 ppm) Maintain 3 - 48 hr	1.28 - 12.8 fl oz/1,000 gal 100 ml - 1 L/10,000 L 1 - 10 ppm ai Treat #120 hr # 4 times per year
Continuous feed	Initial: 0.2 - 1.0 lb/1,000 gal 240 g - 1.2 kg/10,000 L (24 - 120 ppm) Subsequent: 0.02 - 0.2 lb/1,000 gal 24 - 240 g/10,000 L (2.4 - 24 ppm)		
Auxiliary Water/Service Water and Wastewater			
Intermittent or slug	Initial: 1.5 - 4 lb/1,000 gal 1.8 - 4.8 kg/10,000 L for 4 to 8 hr 1 to 4 times/week (180 - 480 ppm) Subsequent: 0.75 - 2 lb/1,000 gal 900 g - 2.4 kg/10,000 L (90 - 240 ppm)	Initial: 0.3 to 1.3 lb/1,000 gal 360 g - 1.56 kg/10,000 L (36 - 156 ppm) for 4 - 8 hr 1 - 4 x/week Subsequent: 0.15 - 0.65 lb/1,000 gal 180 - 780 g/10,000 L 18 to 78 ppm	
Other	Spray onto waste pile	Spray onto waste pile	

(0.05 to 0.5 lb per 1,000 gal of water), 6 to 60 ppm, as needed to maintain control.

(2) Continuous feed method: Initially when fouled, 240 to 1.2 kg per 10,000 L water (0.2 to 1.0 lb per 1,000 gal of water), 24 to 120 ppm. Continue until control is achieved. Subsequently, 24 to 240 g per 10,000 L water (0.02 to 0.2 lb per 1,000 gal of water), 2.4 to 24 ppm.

e. Apply as follows for auxiliary water and wastewater systems:

(1) Intermittent or slug method: 1.8 to 4.8 kg in 10,000 L water (1.5 to 4.0 lb per 1,000 gal of water), 180 to 480 ppm, in system water or in water being added to system, for 4 to 8 hr, 1 to 4 times per week or as needed to achieve control. Subsequently, 900 g to 2.4 kg in 10,000 L water (0.75 to 2.0 lb per 1,000 gal of water), 90 to 240 ppm.

(2) Can be sprayed onto a waste pile.

CT-2 is applied as follows:

a. Rates are given as weight of product, at 960 g L^{-1} (8.0 lb per gal). Concentrations are based on product.

b. Apply as follows for recirculating or once-through cooling water systems: add 20 to 200 g per 10,000 L water (0.016 to 0.166 lb per 1,000 gal of water), 2 to 20 ppm, based on water in the system or on flow rate through the system. Maintain this concentration for 3 to 48 hr.

c. Apply as follows for auxiliary water and wastewater systems:

(1) Intermittent or slug method: 360 - 1.56 kg/10,000 L (0.3 to 1.3 lb per 1,000 gal) of water in system or being added to system, 36 to 156 ppm, for 4 to 8 hr, 1 to 4 times per week or as needed to achieve control. Subsequently, use 180 to 780 g per 10,000 L (0.15 to 0.65 lb per 1,000 gal) of water, 18 to 78 ppm.

(2) Can be sprayed onto a waste pile.

CT-4 is applied as follows:

a. Rates are given as volume of product. Concentrations are based on active ingredient (ai) of quaternary compound (10 percent of product).

b. Apply as follows for once-through freshwater cooling water systems: 100 ml to 1 L per 10,000 L (1.28 to 12.8 fluid ounces per 1,000 gal) of water, 1 to 10 ppm at no more than 4 times per year and for no more than 120 hr per application.

Maximum Water Concentration

The maximum water concentration is designated in a National Pollutant Discharge Elimination System (NPDES) permit for individual facility. Notify the permitting authority in writing prior to discharge.

Notify the local sewage treatment plant authority before discharging effluent containing this product to sewer systems. Contact State Water Board or Regional Office of the U.S. Environmental Protection Agency (USEPA) for guidance.

Segment plantwide applications to reduce the amount of product appearing in effluent.

Use Restrictions

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, ocean or other waters unless in accordance with the requirements of an NPDES permit and notification of the permitting authority in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact the State Water Board or Regional Office of the USEPA.

Effluent inactivation may be required to comply with State and Federal water quality criteria.

Do not use water containing residues from use of CT-2 and CT-4 to irrigate crops used for food or feed.

Use of CT-4 in public/municipal or single- or multiple-family private/residential potable/drinking water systems is strictly prohibited.

Use of CT-4 in any cooling water system that discharges effluent within 1/4 mile of either a public/municipal or single- or multiple-family private/residential potable/drinking water intake is strictly prohibited.

Do not contaminate water, food, or feed by storage or disposal.

Timing and Appearance of Effects

Treatment effects on individual mussels occur within a few days.

It is suggested that sites evaluate treatment effects by taking mussels from system and placing them into bioboxes for monitoring.

Toxicological Data

Sensitivity of nontarget organisms has been studied by Waller et al. (1993).

The Signal Word is DANGER.

The following tabulation lists the toxicology of Clam-Trol formulation:

Aquatic Toxicology of CLAM-TROL Formulations						
	CT-1		**CT-2**		**CT-3**	
Organism	**LC_{50} mg L^{-1}**	**NOEL mg L^{-1}**	**LC_{50} mg L^{-1}**	**NOEL mg L^{-1}**	**LC_{50} mg L^{-1}**	**NOEL mg L^{-1}**
96-hr Flow-Through						
Rainbow trout	8.1	6.5	2	1.2	10	6
Fathead minnow	2.9	2.1	0.72	0.41	4	2
48-hr Flow-Through						
Daphnia magna	0.2	0.135	0.04	0.026	0.2	0.13
Ceriodaphnia	0.14	0.05	N/A		N/A	
96-hr Flow-Through						
Mysid shrimp	0.34	0.1	0.16	0.03	0.8	0.15
Sheepshead minnow	N/A		1.76	1	8.8	5
Menidia beryllina (Silversides)	N/A		0.62	0.35	3.1	1.75
Note: Data from BetzDearborn, Inc., 1998a, 1998b, 1998c.						

Once adsorbed to bentonite clay, ADBAC is not harmful to aquatic organisms, benthic organisms, or microorganisms.

Precautions

This product can be toxic to fish and wildlife depending on dose.

It is corrosive. It causes eye and skin damage and is harmful if swallowed. Do not get into eyes, on skin, or on clothing. Do not inhale vapor or mist. Use with adequate ventilation.

Wear rubber gloves, goggles, or face shield when handling. Immediately remove and wash contaminated clothing before reuse. Wash thoroughly after handling.

Do not use, pour, or store near heat or open flame.

Field Instructions and Guidance on Operational Applications

Badly fouled systems must be cleaned before treatment is begun. Heavy infestations of mollusks should be physically removed by vacuuming, dredging, or scraping prior to Clam-Trol treatment.

A colorimetric field test is available to determine concentration of product in treated water.

Evaluate treatment effects by taking mussels from the system and placing them into bioboxes for monitoring.

CT-1 is compatible with stainless steel, copper alloys, and most common plastics and rubbers. Avoid the use of mild steel, low-density polyethylene, nitrile (Buna N), polyurethane, or Viton in handling the concentrated product.

CT-2 and CT-4 are compatible with all common engineering plastics and elastomers, except nylon. Preferred plastics are polyvinyl chloride, polythylene, and Teflon. Avoid linear high-density polyethylene for storage tanks. Preferred elastomers are butyl rubber, ethylene propylene rubber (ethylene propylene diene monomer) rubber, and natural rubber. Types 304 and 316 stainless steels are suitable for handling at temperatures below 120 ºF (49 ºC). Hastelloy or NMonel should be used instead of stainless steel for applications requiring prolonged exposure to undiluted product at temperatures > 120 ºF (49 ºC).

A listing of compatible feed equipment is available from BetzDearborn, Inc. (1990).

Adjuvant/Detoxicant/Deactivant Use

ADBACs undergo neutralization and detoxification by natural routes, but the process is accelerated by the addition of highly adsorbent, anionically charged materials.

An analytical test procedure to monitor product use and plant outfall levels is available from BetzDearborn, Inc. (1990).

For CT-1, the ammonium chloride quaternary ammonium compound and the DGH are readily neutralized by anionic materials such as clays (bentonite), silts, humic acids, suspended solids and cooling system surfaces. It can be actively detoxified by Betz® DT-1.

CT-2 and CT-4 can be inactivated using Betz DTS or DTG.

Do not discharge CT-4 without performing proper deactivation, using bentonite clay at 5 ppm or more of clay to 1 ppm of product.

Application Techniques

The products can be metered to a system for short application periods, using a suitably sized positive displacement pump.

Make additions of CT-2 to auxiliary water/service water and wastewater systems during the pumping operation and as close to the pump as possible to ensure adequate mixing.

CT-2 and CT-4 can also be metered into a flow of clean dilution water to facilitate use in a distribution header system.

If a closed-loop system can be set up to allow the molluscicide to be recirculated for the required period of time, the volume of chemical required can be significantly reduced.

Warmer water temperatures and longer contact times reduce the concentration of Clam-Trol required for effective treatment.

Recirculating or closed systems should be laid up for 12 to 24 hr after the system is treated. Where possible, blowdown from cooling towers should be suspended for 12 to 24 hr after the system is charged with an effective amount of product.

Segmenting plantwide applications reduces the amount of product that appears in plant effluent.

The product is available in 55-gal (108-L) drums, bulk, or semibulk containers.

Antidote Information

Use the following antidotes:

a. *Contact with skin*: wash immediately with plenty of soap and water. Immediately contact physician.

b. *Contact with eyes*: flush promptly and thoroughly with clear water for at least 15 minutes. Immediately contact physician.

c. *Ingestion*: immediately contact physician.

d. *Notice to physician*: mucosal damage may contraindicate the use of gastric lavage.

e. *Additional*: Measures against circulatory shock, respiratory depression, and convulsion may be needed.

f. *Emergency telephone*: 1-800-877-1940 (BetzDearborn).

References

BetzDearborn, Inc. (1988). “Label: Clam-Trol CT-1.” Trevose, PA. 2 pp.

BetzDearborn, Inc. (1990). “Betz CLAM-TROL® CT-1 molluscicide,” Product Facts PFP 083 9008, Trevose, PA.

BetzDearborn, Inc. (1993a). “Label: Clam-Trol CT-2.” Trevose, PA. 2 pp.

BetzDearborn, Inc. (1993b). “Label: Clam-Trol CT41.” Trevose, PA. 1 p.

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BetzDearborn, Inc. (1998b). “Material Safety Data Sheet: CT-2.” Trevose, PA. 8 pp.

BetzDearborn, Inc. (1998c). “Material Safety Data Sheet: CT-4.” Trevose, PA. 8 pp.

Fisher, S.W., Dabrowska, H., Waller, D. L., Babcock-Jackson, L., and Zhang, X. (1994). “Sensitivity of zebra mussel (*Dreissena polymorpha*) life stages to candidate molluscicides,” *J. Shellfish Res*. 13: 373-377.

Waller, D. L., Rach, J. J., Cope, W. G., Marking, L. L., Fisher, S. W., and Dabrowski, H. (1993). “Toxicity of candidate molluscicides to zebra mussels (*Dreissena polymorpha*) and selected nontarget organisms,” *J. Great Lakes Res*. 19, 695-702.

MACROTROL 9210

MACROTROL 9210 and the more concentrated NALCO 9380 are water-soluble quaternary ammonium-based products of the n-alkyl dimethyl benzyl ammonium chloride type. They have penetrating and dispersing characteristics and act as nonoxidizing biocides. They are labeled for use in a wide range of water systems where they can control macroorganisms such as mollusks, clams, and barnacles, as well as microfoulants such as bacteria, fungi, and algae (Dobbs et al. 1995). They are effective in seawater as well as freshwater systems. Excess residues of NALCO 9380 and MACROTROL 9210 must be deactivated or detoxified prior to treated water discharge to a receiving stream.

Monitoring kits for use in checking zebra mussel veliger density and settling in a water system and experimental systems for determining adult mussel mortality under local water quality conditions are available from the source, Nalco Chemical Company (address given in next section).

Chemical Name and Commercial Formulations

These products have the following characteristics:

a. *Chemical name*: Ammonium chlorides

b. *Formulations*:

(1) MACROTROL™ 9210

- 5 percent alkyl (60 percent C14, 30 percent C16, 5 percent C12, 5 percent C-18) dimethyl benzyl ammonium chloride
- 5 percent alkyl (68 percent C12, 32 percent C14) dimethyl ethylbenzyl ammonium chlorides
- Liquid
- EPA Reg. No. 6836-57-1706

(2) NALCO® 9380

- 40 percent alkyl (60 percent C14, 30 percent C16, 5 percent C12, 5 percent C-18) dimethyl benzyl ammonium chloride
- 40 percent alkyl (68 percent C12, 32 percent C14) dimethyl ethylbenzyl ammonium chloride
- Liquid
- EPA Reg. No. 6836-234-1706

c. *Source*: Nalco Chemical Company
One Nalco Center
Naperville, IL 60563-1198
(630) 305-1000
Emergencies: 1-800-462-5378

Mode of Action

These products are corrosive to membranes, interfere with respiration, and are fast-acting.

Application Strategies

Use continuous or intermittent feed, depending on degree of system fouling and retention time. They can be applied off-line or on-line.

Use initial treatment to remove mussels from system, and follow with treatments as needed to maintain control.

The primary type of treatment program recommended for controlling zebra mussels with these products is eradication, to eliminate accumulated mussels.

Timing of Application

When system is noticeably fouled, apply to achieve control.

Monitor system to determine when to use subsequent treatments to maintain control.

For eradication, apply one to three times per year during warm season. Generally, apply immediately after the annual peak in reproduction (typically in June or July) and at the end of the season (October or November) (Nalco 1996a).

Application Rates

MACROTROL 9210. Note: Excess residual MACROTROL 9210 must be detoxified prior to discharge to a receiving stream by using the proprietary compound NALCO 1315 or by using bentonite clay at a minimum ratio of 5 ppm clay to 1 ppm product (Nalco 1995a).

a. *In recirculating, auxiliary cooling water, and wastewater systems:*

(1) *Initial dose:* Add 0.08 to 0.8 lb per 1,000 gal water (10 to 100 ppm: 100 to 1,000 kg per 10,000 L). Repeat as necessary to achieve control.

(2) *Subsequent dose:* When control is evident, add 0.08 to 0.4 lb per 1,000 gal (10 to 50 ppm: 100 to 500 kg per 10,000 L), as needed to maintain control.

b. In once-through cooling water systems:

(1) Intermittent feed:

- *Initial dose:* When the system is noticeably fouled, add 0.08 to 0.8 lb per 1,000 gal water (10 to 100 ppm: 100 to 1000 kg per 10,000 L), based on system flow rates. The minimum treatment period should be 6 to 24 hr. Repeat as necessary to achieve control.

- *Subsequent dose:* When control is evident, add 0.04 to 0.4 lb per 1,000 gal (5 to 50 ppm: 50 to 500 kg per 10,000 L), based on system flow rates on an as-needed basis to maintain control. Frequency of feed should be tied to a monitoring program.

(2) Continuous feed:

- *Initial dose:* When the system is noticeably fouled, add 0.04 to 0.4 lb per 1,000 gal water (5 to 50 ppm: 50 to 500 kg per 10,000 L), based on system flow rates. Continue to feed until needed control is achieved.

- *Subsequent dose:* Maintenance control can be effective through continuous feed at 0.016 to 0.16 lb per 1,000 gal (2 to 20 ppm: 20 to 200 kg per 10,000 L), based on system flow rates.

NALCO 9380. Note: NALCO 9380 must be deactivated prior to discharge from the system by using bentonite clay at a minimum ratio of 5 ppm clay to 1 ppm product or by using the proprietary compound NALCO 1315 (Nalco 1995b).

a. In recirculating, auxiliary cooling water, and wastewater systems:

(1) *Initial dose:* Add 0.2 to 1.7 fluid ounces per 1,000 gal water (1 to 12 ppm: 10 to 120 ml per 10,000 L). Repeat as necessary to achieve control.

(2) *Subsequent dose:* When control is evident, add 0.2 to 0.9 fluid ounces per 1,000 gal (1 to 6 ppm: 10 to 60 ml per 10,000 L), as needed to maintain control.

b. In once-through cooling water systems:

(1) Intermittent feed:

- *Initial dose:* When the system is noticeably fouled, add 0.2 to 1.7 fluid ounces per 1,000 gal water (1 to 12 ppm: 10 to 120 ml per 10,000 L) based on system flow rates. The minimum treatment period should be 6 to 24 hours. Repeat as necessary to achieve control.

- *Subsequent dose:* When control is evident, add 0.1 to 0.9 fluid ounce per 1,000 gal (0.6 to 6 ppm: 6 to 60 ml per 10,000 L), based on system flow rates on an as-needed basis to maintain control. Frequency of feed should be tied to a monitoring program.

(2) Continuous feed:

- *Initial dose:* When the system is noticeably fouled, add 0.1 to 0.9 fluid ounce per 1,000 gal (0.6 to 6 ppm: 6 to 60 ml per 10,000 L), based on system flow rates. Continue to feed until needed control is achieved.
- *Subsequent dose:* Maintenance control can be effective through continuous feed at 0.03 to 0.3 fluid ounces per 1,000 gal (0.2 to 2.5 ppm: 2 to 25 ml per 10,000 L), based on system flow rates.

Maximum Water Concentration

Discharge concentrations of these products only in accordance with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit. Notify the permitting authority in writing prior to discharge. Notify the local sewage treatment plant authority before discharging effluent containing this product to sewer systems. For guidance, contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Excess residues of NALCO 9380 and MACROTROL 9210 must be detoxified prior to discharge.

Use Restrictions

Do not apply to potable or domestic water systems. Use in public or private potable water systems is strictly prohibited. Use in any cooling water system that discharges effluent within 0.25 mile of either a public or private potable water intake is prohibited.

Do not use water containing residues from use of this product to irrigate crops used for food or feed.

This product is toxic to fish and aquatic organisms at certain concentrations. Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System permit and notification of the permitting authority in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance, contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Excess residues of NALCO 9380 and MACROTROL 9210 must be detoxified prior to discharge. Deactivation is conducted by using bentonite clay at a minimum ratio of 5 ppm clay to 1 ppm product, or the product NALCO 1315.

NALCO 9380 cannot be sold or used in the State of California.

Timing and Appearance of Effects

Effects on respiratory activity of adult zebra mussels are seen within 24 hr (Nalco 1996a).

Toxicological Data

The Signal Word is Danger.

Toxicity is shown in the following tabulations:

Aquatic Toxicity of MACROTROL 9210 Using the 96-hr Static Acute Test	
Organism	**LC_{50}, mg L^{-1}**
Mysid shrimp	0.9
Bluegill sunfish	5.2
Rainbow trout	9.3
From Nalco (1998).	

Aquatic Toxicity of NALCO 9380 Using the 96-hr Static Acute Test	
Organism	**LC_{50}, mg L^{-1}**
Mysid shrimp	0.115
Bluegill sunfish	0.644
Rainbow trout	1.162
From Nalco (1996b).	

Precautions

This product is corrosive and harmful or fatal if swallowed.

It causes eye damage and skin irritation. Do not get in eyes, on skin, or on clothing. Wear goggles or face shield and rubber gloves when handling. Remove and wash contaminated clothing before reuse.

Field Instructions and Guidance on Operational Applications

After this product is used, it must be deactivated prior to discharge from the system using bentonite clay or the proprietary compound NALCO 1315 at a minimum ratio of 5 ppm clay to 1 ppm product.

Do not store the container on its side. Avoid creasing or impacting sidewalls of container.

Storage tanks should be constructed of polyvinyl chloride (PVC), carbon steel, or containers lined with Plasite 6000 or Plasite 7122. Feed lines and pumps should be constructed of PVC, Hypalong, Viton, Teflon, Buna-N, polypropylene, plexiglass, polyurethane, carbon steel, 304 stainless steel, or 316 stainless steel.

Adjuvant/Detoxicant/Deactivant Use

Excess residual MACROTROL 9210 and NALCO 9380 not deactivated by natural solids or turbidity in water must be detoxified prior to discharge to a receiving stream using the proprietary compound NALCO 1315 (a stabilized clay slurry) or bentonite clay at a minimum ratio of 5 ppm clay to 1 ppm product.

Feed clay continuously to the outfall to ensure maximum distribution and mixing with the water to be detoxified.

Application Techniques

Apply with a metering pump.

Apply at feed point as far upstream as possible to allow exposure to maximum number of mussels.

Antidote Information

Use the following antidotes:

a. *Eyes*: immediately flush with plenty of water for at least 15 minutes. Call a physician.

b. *Skin*: flush with plenty of water for at least 15 minutes.

c. *If swallowed*: drink a large quantity of milk, egg whites, or gelatin solution; if these are not available, drink large quantities of water. Avoid alcohol. Call a physician immediately.

d. *Note to physician*: probable mucosal damage may contraindicate the use of gastric lavage.

References

Dobbs, M. G., Cherry, D. S., Scott, J. C., and Petrille, J. C. (1995). "Environmental assessment of an alkyl dimethyl benzyl ammonium chloride (ADBAC) based molluscicide using laboratory tests." *Proceedings, Fifth International Zebra Mussel and Other Aquatic Nuisance Organisms Conference*, Toronto, Canada, February 14-21, 1995. The Professional Edge, Pembroke, Ontario, Canada, 87-101.

Nalco. (1995a). "MACROTROL 9210: Label," Nalco Chemical Company, Chicago, IL, 1 p.

Nalco. (1995b). "Nalco 9380: Label," Nalco Chemical Company, Chicago, IL, 1 p.

Nalco. (1996a). "Control of zebra mussels: Program profile," Nalco Chemical Company, Naperville, IL, 5 pp.

Nalco. (1996b). "Material safety data sheet: NALCO 9380," Nalco Chemical Company, Chicago, IL, 9 pp.

Nalco. (1998). "Material safety data sheet: NALCO 9210," Nalco Chemical Company, Chicago, IL, 9 pp.

VeliGON

High-charge cationic coagulant dimethyl diallyl ammonium chloride (DMDAAC) compounds have been used in water treatment plants as flocculators and clarification aids (Blanck, Mead, and Adams 1996), and have become the first molluscicide approved by the U.S. Environmental Protection Agency for use in domestic potable water systems. The various VeliGON formulations of these compounds differ in their molecular weight and cationic charge density. Floc allows settling out of veligers, and affects adults (Waller et al. 1993). The use of this compound in water treatment plants at concentrations for zebra mussel and *Corbicula* veliger control has been shown to reduce or eliminate the amount of alum coagulant required at the rapid mix area. This aids liquid/solid separation operations, resulting in less residual solids and soluble aluminum (sludge) in the plant effluent, and higher pH of finished water. The reduction in alum usage can improve the stability index and allow longer filter runs. Individual users must obtain specific discharge permits.

Chemical Name and Commercial Formulations

This compound has the following characteristics:

a. Active ingredient: poly (dimethyl diallyl ammonium chloride)

b. Synonyms: DMDAAC, pDADMAC, DDDMAC, DMDACC

c. Formulations:

(1) VeliGON™ CL-M

- 39.8 percent poly (dimethyl diallyl ammonium chloride); liquid
- EPA Registration No. 10445-115

(2) VeliGON™ DL-M

- 17.5 percent poly (dimethyl diallyl ammonium chloride); liquid
- EPA Registration No. 10445-121

(3) VeliGON™ L-M

- 19.8 percent poly (dimethyl diallyl ammonium chloride); liquid
- EPA Registration No. 10445-116

(4) VeliGON™ LS-M

- 10 percent poly (dimethyl diallyl ammonium chloride); liquid
- EPA Registration No. 10445-117

(5) VeliGON™ TL-M

- 19.8 percent poly (dimethyl diallyl ammonium chloride); liquid
- EPA Registration No. 10445-118

(6) VeliGON™ T-2-M

- 33 percent poly (dimethyl diallyl ammonium chloride); liquid
- EPA Registration No. 10445-122

d. *Source*: Calgon Corporation
P.O. Box 1346
Pittsburgh, PA 15230-1346
(412) 777-8000
Health and Environmental Affairs: (412) 494-8000
Emergency: (412) 494-8000
For information, jim.farmerie@ecc.com.

Mode of Action

These quaternary ammonium compounds are aqueous solutions of medium [to low] molecular weight high-charge cationic polymers. They are flocculants and coagulants and produce a dense floc that works to prevent settling of zebra mussel veligers. They also affect adults, and it is suggested that these do not attach as firmly under treatment.

Application Strategies

Continuously feed during the spawning season at the intake of the raw water source.

The VeliGON compounds are approved for use in potable water treatment plant systems but can be applied only in a system where there is a treatment plant that includes a filter.

Timing of Application

Apply during the breeding season, when veligers are present in intake water due to mussel spawning activities. This varies by location. In the northeastern United States, spawning begins in the spring and continues through the summer.

Onsite monitoring is usually required to determine the start and duration of the spawning period in an area in order to optimize treatment timing.

Application Rates

Apply at a rate of 1 to 5 ppm on a continuous basis during the spawning/breeding season.

The various VeliGON compounds differ in molecular weight and cationic charge density. Choice of the most suitable product and determination of the application rate required for local water treatment systems is usually based on local veliger monitoring and optimal clarification effect in an on-site bench-scale test (jar test) under local water and site conditions.

DMDAAC has been shown to have a median lethal concentration LC_{50} at 96 hr for adult zebra mussels at between 1.5 and 3.0 mg L^{-1} (ppm) (Blanck, Mead, and Adams 1996).

The following tabulation lists the treatment rates for VeliGON formulatons:

Treatment Rates for VeliGON Formulations[1]

Product	Treatment to Intake Water	Concentration of Active Ingredient, ppm
VeliGON CL-M	0.3 to 3.3 fluid ounces per 1,000 gal 9 to 98 ml per 378,500 L	1 to 10
VeliGON DL-M	0.68 to 6.8 fluid ounces per 1,000 gal 20 to 200 ml per 378,500 L	1 to 10
VeliGON L-M	0.6 to 6.6 fluid ounces per 1,000 gal 18 to 195 ml per 378,500 L	1 to 10
VeliGON LS-M	1.2 to 13.2 fluid ounces per 1,000 gal 35.5 to 390 ml per 378,500 L	0.1 to 1
VeliGON TL-M	0.6 to 6.6 fluid ounces per 1,000 gal 18 to 195 ml per 378,500 L	1 to 10
VeliGON T-2-M	0.36 to 3.6 fluid ounces per 1,000 gal 11 to 106 ml per 378,500 L	1 to 10

[1]From product labels (Calgon Corporation 1995a, b, c, d, 1996a, b)

Maximum Water Concentration

Apply VeliGON products only in systems with a treatment plant that includes a filter.

Discharge into lakes, streams, ponds, or public waters only in accordance with the requirements of a National Pollutant Discharge Elimination System permit. Notify the permitting authority in writing prior to discharge.

Limit residues of poly (N,N-dimethyl diallyl ammonium chloride) in finished potable water to no more than 50 ppm (50 mg L^{-1}).

The VeliGON products are certified by the National Sanitation Foundation International to American National Standards Institute/National Sanitation Foundation (ANSI/NSF) Standard 60-1997 (ANS/NSF 1997) for use in potable water as coagulation and flocculation drinking water treatment chemicals to these maximum doses/feed rates:

a. VeliGON CL-M: 25 mg L^{-1}

b. VeliGON DL-M: 57 mg L^{-1}

c. VeliGON L-M: 50 mg L^{-1}

d. VeliGON LS-M: 100 mg L^{-1}

e. VeliGON TL-M: 50 mg L^{-1}

f. VeliGON T-2-M: 23.8 mg L^{-1}

pDADMAC is certified to ANSI/NSF 60-1997.

Use Restrictions

Apply VeliGON products only in systems with a treatment plant that includes a filter.

This pesticide is toxic to fish and aquatic invertebrates. Do not use in facilities discharging directly or indirectly to estuarine or marine environments.

Do not discharge into lakes, streams, ponds, or public waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System permit and notification of the permitting authority in writing prior to discharge.

Do not discharge effluent containing this product into sewage systems without previously notifying the local sewage treatment plant authority. For guidance contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Residues of poly (N,N-dimethyl diallyl ammonium chloride) in finished potable water should be no more than 50 ppm (50 mg L^{-1}).

Do not contaminate water, food, or feed by storage or disposal.

Timing and Appearance of Effects

Significant treatment effects on individuals are seen within 3 days.

Toxicological Data

Note: LC_{50} determinations without added suspended solids overestimate the true toxicity of cationic polymers. Suspended solids and other dissolved organic materials like humic acid are present in many natural waters, and reduce the effective concentration of the polymer and thereby its toxicity. A reduction in toxicity is observed as shown in the following tabulation under turbid conditions (Calgon 1995e-h, 1996c,d).

Aquatic Toxicity Data for a 40 percent Solution of Poly(dimethyl diallyl ammonium chloride)		
Organism	**Test**	**Toxicity, mg L^{-1} (ppm)**
Bluegill sunfish	96 hr LC_{50}	0.82 - 1.3
Rainbow trout	96 hr LC_{50}	0.37
Daphnia magna	48 hr LC_{50}	0.99 (in clear water)
		1.2 - 2.5 (in 50-ppm clay suspension)
		24.8 (in 1,000-ppm clay suspension)

Precautions

These products are not expected to cause eye or skin irritation, or to be toxic if swallowed. However, avoid contact with skin, eyes, or clothing. In case of contact, immediately flush eyes or skin with plenty of water. Get medical attention if irritation persists.

Use goggles; otherwise, no special personal protective equipment is required.

Field Instructions and Guidance on Operational Applications

Full-scale applications of VeliGON may allow greater reduction of primary coagulant than indicated in short, bench-scale preliminary tests due to longer time in the system.

Protect products from low temperatures. Maintain at 38 ºF (3 ºC) or higher. Store in heated buildings or heat-traced tanks to prevent freezing. Although products are freeze-thaw stable, stratification may occur upon freezing; they will become homogeneous again upon agitation.

The product is noncorrosive at use concentrations, but the undiluted product is moderately corrosive to iron and copper, including their alloys. Avoid exposing to carbon steel or copper. Do not store in stainless steel.

Storage tanks, chemical feed systems, and piping should be of high-density (HDPE) or cross-linked (XLPE) polyethylene, fiberglass (FRP) with polyester or vinylester resins, epoxy, or vinylester-lined steel. Pump liquid ends and piping should be constructed of polyethylene, propylene, polyvinyl chloride, chlorinated polyvinyl chloride, Kynar, 316 stainless steel, Viton, or Hypalon. Refer to manufacturer's recommendations.

Adjuvant/Detoxicant/Deactivant Use

None required.

Application Techniques

VeliGON may be metered into the flow and may be fed undiluted as long as in-line dilution is provided. Dilution to 1 percent as product is recommended to assure better contact of the coagulant with impurities in the water. Feed systems for undiluted material should be capable of handling 5,000-cps viscosity material. A Calgon SD, P-18, or MDS feed system is recommended by the manufacturer.

Addition of products should occur at a point sufficiently inside the intake pipe to prevent any release of VeliGON into the intake source (5 to 10 ft or 1.5 to 3 m for normal flow operations).

Addition should be made through a supply line placed inside the intake pipe or in some locations that will ensure that no contamination of public water occurs in the event of a break.

Feed exits must be equipped with a pressure check valve at the feed line exit to seal the feed line when intake flow stops.

Feed pumps must be designed to shut down when intake pumps stop. Planned shutdowns shall require feed pumps to be stopped 1/2 hr prior to shutdown.

Antidote Information

Use the following antidotes:

a. If swallowed: do not induce vomiting. Drink large quantities of water.

b. If in eyes: flood eyes with water for at least 15 minutes.

c. If on skin: wash thoroughly with soap and water.

d. 24-hour emergency telephone: (412) 494-8000 (Calgon Corporation).

References

American National Standards Institute/National Sanitation Foundation. (1997). "Drinking water treatment chemicals - health effects," ANSI/NSF 60-1997, Ann Arbor, MI.

Blanck, C. A., Mead, D. F., and Adams, D. J. (1996). "Effective control of zebra mussels using a high molecular weight polymer." Abstract from the *Sixth International Zebra Mussel and Other Aquatic Nuisance Species Conference*, Dearborn, MI, March 1996.

Calgon Corporation. (1995a). "Label: VeliGON CL-M," Pittsburgh, PA. 1 p.

Calgon Corporation. (1995b). "Label: VeliGON L-M," Pittsburgh, PA. 1 p.

Calgon Corporation. (1995c). "Label: VeliGON LS-M," Pittsburgh, PA. 1 p.

Calgon Corporation. (1995d). "Label: VeliGON TL-M," Pittsburgh, PA. 1 p.

Calgon Corporation. (1995e). "Material Safety Data Sheet: VeliGON CL-M," Pittsburgh, PA. 6 pp.

Calgon Corporation. (1995f). "Material Safety Data Sheet: VeliGON L-M," Pittsburgh, PA. 6 pp.

Calgon Corporation. (1995g). "Material Safety Data Sheet: VeliGON LS-M," Pittsburgh, PA. 6 pp.

Calgon Corporation. (1995h). "Material Safety Data Sheet: VeliGON TL-M," Pittsburgh, PA. 6 pp.

Calgon Corporation. (1996a). "Label: VeliGON DL-M," Pittsburgh, PA. 1 p.

Calgon Corporation. (1996b). "Label: VeliGON T-2-M," Pittsburgh, PA. 1 p.

Calgon Corporation. (1996c). "Material Safety Data Sheet: VeliGON DL-M," Pittsburgh, PA. 6 pp.

Calgon Corporation. (1996d). "Material Safety Data Sheet: VeliGON T-2-M," Pittsburgh, PA. 6 pp.

Waller, D. L., Rach, J. J., Cope, W. G., Marking, L. L., Fisher, S. W., and Dabrowski, H. (1993). "Toxicity of candidate molluscicides to zebra mussels (*Dreissena polymorpha*) and selected nontarget organisms," *J. Great Lakes Res.* 19, 695-702.

Aromatic Hydrocarbons

These compounds are ring-structure organics with film-forming and surfactant activity and include formulations that have been used as biocides in industrial water-handling systems for many years.

BULAB 6009

This aromatic hydrocarbon product is used to control algae, bacteria, and fungi in industrial recirculating cooling water systems and to protect wood against dry or wet rot in cooling water towers. It is also used to prevent microorganism fouling in the petroleum industry.

Chemical Name and Formulations

This product has the following characteristics:

a. Chemical name: 2-(Thiocyanomethylthio)benzothiazole; known as TCMTB.

b. Formulation:

- BULAB® 6009

- 30 percent TCMTB; dispersable in water

c. EPA Reg. No.: 1448-55

d. Source: Buckman Laboratories, Inc.
1256 McLean Blvd.
Memphis, TN 38108
(901) 278-0330
1-800-BUCKMAN

Mode of Action

BULAB 6009 is corrosive to membranes. While some avoidance of the compound via shell closure has been seen, the majority of zebra mussels continue siphoning in the presence of TCMTB (McMahon, Shipman, and Long 1993).

Application Strategies

Treat waters of whole system periodically.

Timing of Application

Maintain concentrations during season of activity.

Application Rates and Duration

Use of 1 to 6 mg L^{-1} BULAB 6009 for once-through systems is the rate recommended for control of Asiatic clam, *Corbicula fluminea* (Electric Power Research Institute 1993).

The following tabulation summarizes laboratory studies showing efficacies of this product and the relationship of exposure time to concentration.

Activity of BULAB 6009 on Zebra Mussel

Concentration mg L^{-1}	LT_{50}, hr		LT_{100}, hr		MTD, hr	
	MMB	MSL	MMB	MSL	MMB	MSL
0.5	92	652	192	758	108	659
1.0	74	336	144	485	89	335
2.0	70	221	144	313	91	228
4.0	78	184	110	260	85	189

Note: MNB = Martin, Mackie, and Baker (1993)
MSL = McMahon, Shipman, and Long (1993)
LT_{50}, LT_{100} = time to percent mortality
MTD = mean time to death

Maximum Water Concentration

Discharge effluent containing this product only in accordance with the requirements of a National Pollutant Discharge Elimination System permit. Notify the permitting authority in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance, contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Except for treatment purposes, do not apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high-water mark.

Use Restrictions

This pesticide is toxic to fish.

Do not use in offshore or estuarine operations. In terrestrial uses, do not apply directly to open water, to areas where surface water is present, or to intertidal areas below the mean high-water mark.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System permit and written notification of the permitting authority prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance, contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Timing of Effects

Treatment effects are seen in 4 to 10 days (see previous tabulation).

Toxicological Data

BULAB 6009 is highly toxic to fish (Waller et al. 1993) (as shown in the following tabulation).

The Signal Word is Danger.

Toxicity of BULAB 6009

Organism	Test	Acute Aquatic Median Lethal Concentration, mg L^{-1}
Daphnia magna	48 hr	0.07
Fathead minnow	96 hr	0.037
Rainbow trout	96 hr	0.117

Precautions

Do not use or store near heat or open flame. Do not expose to extreme temperatures.

This product is corrosive to eyes, skin, and mucous membranes. Do not get in eyes, on skin, or on clothing. It causes irreversible eye damage. It also causes skin irritation, and may cause allergic skin reactions. It is harmful if swallowed.

Wear goggles or face shield and rubber gloves when handling. Wash thoroughly with soap and water after handling. Remove contaminated clothing and wash before reuse.

Field Instructions and Guidance on Operational Applications

Do not stack containers more than five drums high.

Do not heat or store above 122 ºF (50 ºC).

Drums should be opened in well-ventilated areas. Overpack leaking or damaged drums.

Spills should be absorbed in sawdust or sand and disposed of in a sanitary landfill. Keep container closed when not in use.

Adjuvant/Detoxicant/Deactivant Use

None required.

Application Techniques

Feed product at a point of strong agitation to ensure mixing.

Antidote Information

Use the following antidotes:

a. *If in eyes*: flush with plenty of water. Get medical attention.

b. *If on skin*: wash with plenty of soap and water. Get medical attention.

c. *If swallowed*: promptly drink a large quantity of milk, egg whites, or gelatin solution; if these are not available, drink large quantities of water. Avoid alcohol. Get medical attention.

d. *Note to physician*: no specific antidote is known. Probable mucosal damage may contraindicate gastric lavage. Treat symptoms.

e. *24-hour emergency number*: 901/767-2722.

References

Electric Power Research Institute. (1993). "Hazard identification of commercially available biocides to control zebra mussels and Asiatic clams," TR-103175, Syracuse Research Corporation, Syracuse, NY.

Martin, I. D., Mackie, G. L., and Baker, M. A. (1993). "Control of the biofouling mollusc, *Dreissena polymorpha* (Bivalvia: Dreissenidae), with sodium hypochlorite and with polyquaternary ammonia and benzothiazole compounds," *Archives of Environmental Contamination and Toxicology* 24, 381-388.

McMahon, R. F., Shipman, B. N., and Long, D. P. (1993). *Zebra mussels: Biology, impacts and control*. T. F. Nalepa and D. W. Schloesser, ed., Lewis Publishers, Boca Raton, FL, 575-598.

Waller, D. L., Rach, J. J., Cope, W. G., Marking, L. L., Fisher, S. W., and Dabrowski, H. (1993). "Toxicity of candidate molluscicides to zebra mussels (*Dreissena polymorpha*) and selected nontarget organisms," *J. Great Lakes Res.* 19, 695-702.

MEXEL 432

This mixture of aliphatic amine surfactants is an anti-fouling material that acts as a corrosion inhibitor and scale dispersant as well as having activity against freshwater and saltwater mussels and barnacles (Giamberini, Czembor, and Pihan 1994; Krueser, Vanlaer, and Damour 1997). It adsorbs to exposed surfaces and forms a protective anti-fouling film on internal components when present in circulating water. Once the material is adsorbed to a surface, it remains in place until it degrades, and this minimizes its presence in outfall.

Chemical Name and Formulations

This product has the following characteristics:

a. *Chemical name*: (Alkylamino)-3 aminopropane

b. *Formulation*:

- MEXEL® 432

- 1.7 percent (Alkyl amino)-3 aminopropane active ingredient (alkyl as in fatty acids of coconut oil); liquid

- 8.08 lb per gal; 970 g per L

c. *U.S. Distributor*: RTK Technologies, Inc.
P.O. Box 86622
Baton Rouge, LA 70879-6622
(225) 755-2194
RTKT1@aol.com
http://www.mexel.fr/mexel432.htm
EPA Registration No. 69100-1

Mode of Action

This hydrocarbon compound is a mixture of aliphatic hydrocarbons, with alcohol and amine functionality, in an aqueous emulsion. The amines act as surfactants, or “filming amines,” and adhere to wetted metal, plastic, concrete, and glass surfaces to form a film through which biofouling organisms cannot form an attachment. This preventive activity deters mussel infestation by repelling veliger settlement and adhesion to clean surfaces. The product gradually kills zebra mussels already in place by retarding byssal thread formation, adhering to and damaging gill surface membranes, and dispersing mussels. Thus, it prevents new infestations and gradually disperses existing infestations, and is used primarily to prevent infestations in a previously cleaned system.

Efficacy is due to presence on system surfaces, not in bulk water flow.

Application Strategies

This product is used for control of mollusks, including zebra mussels and clams, in nonpotable industrial water systems.

It is effective as an acute toxicant for systems that do not have continuous water flow (i.e., fire protection systems, standby facilities), but the preferred use is in closed delivery systems with daily dosage at sublethal levels.

Sites of application do not include freshwater cooling tower systems.

It may be applied to maintain clean systems or to treat systems that are already fouled. The system to be treated should first be cleaned of adult zebra mussels and then treated.

Treatment is usually on an intermittent basis, with normal frequency being once per day, or as needed to maintain control. Intermittent injection of low concentrations has been shown to have the potential for reducing molluscicide quantities while maintaining effectiveness (Giamberini, Czembor, and Pihan 1994).

Timing of Application

Initial application early in the season prior to veliger settlement is most effective, with continuation of daily dosing throughout warm weather.

Application Rate

Note: Dosage is a function of surface area rather than of water flow. See product label (Mexel S.A 1997b).

Standard dosage is for a short period each day, typically 4 ppm for 20 min per day.

Daily dose is determined by the amount of internal surface area to be protected and is calculated at approximately 0.033 lb or 15 g per day (1 lb or 454 g per month) per 100 ft^2 (9.3 m^2) of surface area. Inject dose into circulating water at a rate to achieve a concentration of 1 to 4 ppm: 1 to 4 pints of product for each 125,000 gal of water, or 1 to 4 L per 1,000,000 L water.

A dose of 12 mg L^{-1} per day in flow-through inhibits veliger settling.

Maximum Water Concentration

Do not discharge into environment or public waters.

Dosage in an operating system may be optimized to eliminate detectable concentrations in the effluent.

Use Restrictions

This pesticide is toxic to fish. Do not discharge into lakes, streams, ponds, or public waters unless in accordance with a National Pollutant Discharge Elimination System Permit. Do not flush to sewers. For guidance, contact the Regional Office of the U.S. Environmental Protection Agency.

Do not contaminate water, food, or feed by storage or disposal.

Timing of Effects

Treatment shows effects within a few days, but continuing treatment is required. Monitor treatment efficacy with bioboxes located at critical points in the system.

Toxicological Data

The Signal Word is Danger.

Note: Intermittent dosing at sublethal concentrations means that only organisms that remain within the treated system are at risk. The following tabulations list the aquatic toxicology for static and acute tests, respectively.

Aquatic Toxicology in Static Renewal Tests of MEXEL 432 Using Lake Superior Water Amended with 4.5 mg L^{-1} Humic Acids (mg L^{-1} = ppm)

Organism	Test	Median Lethal Concentration, mg L^{-1}
Rainbow trout	96-hr	11.0
Daphnia magna	48-hr	3.4
Fathead minnow	96-hr	8.06
Note: Data from Mexel S.A 1997a		

Aquatic Toxicology of MEXEL 432 in Acute Tests of Short Daily Exposures

Organism	Daily Exposure, min	Median Lethal Concentration, mg L^{-1}
Daphnia magna	5	26.9
	20	7.2
	80	3.0
Fathead minnow	5	13.1
	20	6.2
	80	2.8
Note: Data from Mexel S.A 1997a		

Precautions

MEXEL 432 is corrosive to skin, eyes, etc. It causes serious burns and is harmful if ingested.

Wear protective clothing, impermeable gloves, safety glasses plus goggles, or a face shield when handling undiluted product. Wash contaminated clothing thoroughly.

Field Instructions and Guidance on Operational Applications

Monitor treatment efficacy with bioboxes located at critical points in the system.

Do not store in low-density polyethylene, polypropylene, or copper, zinc, aluminum, and their alloys.

Store on impermeable surfaces within retention basin.

Avoid any discharge onto the ground. Protect sewers from possible discharges.

Monitor the presence of MEXEL 432 with colorimetric tests of grab samples, or with an electrode (Corroprobe®) measuring free corrosion potential as electrical potential.

Required dosage varies with the solids content of the water and with the temperature. When seasonal water turbidity is high, dosage may need to be increased; dosage may be reduced when water is cleaner. Colder water may require decreased dosage due to slower biodegradation rates. Biodegradation increases with increasing temperature and oxygen availability, and can be accelerated by agitation and by aeration.

Adjuvant or Detoxicant Use

No detoxification is required.

Application Techniques

Standard practice is to dose a system once a day, introducing MEXEL 432 into the water inlet with a metering pump for as long as it takes to inject the daily dosage, i.e., to produce a concentration of 1 to 4 ppm in the system. Under these conditions the product will not be present in the effluent in detectable concentrations.

Use a metering pump near a water inlet to pump the product into a small line that extends down to the inlet area of the main waterline, where it is dispersed into the inlet water stream. The metering pump may be interlocked with the main water pumps to eliminate the possibility of the product entering the environment in the event of reduced water flow. Inject product as near as possible to the inlet in order to protect as much of the inlet piping as possible.

Antidote Information

Use the following antidotes:

a. *Eyes*: hold eyelids open and flush with water. Wash with 0.5 percent acetic acid solution, and then rinse with water for 15 minutes. Consult an ophthalmologist.

b. *Skin*: wash with 2 percent acetic acid solution, then with plenty of soap and water. Get medical attention.

c. *If swallowed*: call a doctor or get medical attention. Do not induce vomiting. Promptly drink a large quantity of milk, egg whites, gelatin solution, or if these are not available, a large quantity of water. Avoid alcohol.

References

Giamberini, L., Czembor, N., and Pihan, J. (1994). "Effects of MEXEL 432 on the settling, detachment and mortality of adult zebra mussels." *Proceedings of The Fourth International Zebra Mussel Conference*, Madison, WI, March 7-10, 1994. University of Wisconsin Sea Grant Institute.

Krueser, R. T., Vanlaer, A., and Damour, A. (1997). "A novel molluscicide, corrosion inhibitor and dispersant," Paper No. 97409, *Proceedings of Corrosion/97*, New Orleans, LA, March 1997. National Association of Corrosion Engineers, Houston, TX, 409/1-409/7.

Mexel S.A (1997a). "Material Safety Data Sheet: MEXEL® 432/0." 5 pp.

Mexel S.A (1997b). "MEXEL 432. Label." 3 pp.

Endothall

The amine salt of the compound endothall, 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, has been used as a herbicide (HYDROTHOL) against submersed weeds in aquatic environments for a number of years, and its effects on aquatic systems are well understood. It has recently been found to be effective against zebra mussels, and a formulation has been registered as EVAC™ for molluscicidal use.

EVAC™

This formulation of endothall is similar to that of the HYDROTHOL 191 aquatic herbicide. However, only EVAC is registered for molluscicide use (Calgon Corporation 1998b). There is no requirement for a holding period or deactivation prior to discharge.

Chemical Name and Formulations

This formulation has the following characteristics:

a. *Active ingredient*: Mono(N,N-dimethylalkylamine) salt of endothall (7-oxabicyclo[2.2.1]- heptane-2,3-dicarboxylic acid)

b. *Formulation of EVAC biocide:*

- 53.0 percent active ingredient, amine salt of endothall (23.36 percent acid equivalent endothall)
- 2 lb technical endothall per gal (240 g per liter)
- Liquid concentrate, soluble in water
- EPA Registration No. 4581-380-10445

c. *Source*: Calgon Corporation
P.O. Box 1346
Pittsburgh, PA 15230-1346
(412) 777-8000
Health and Environmental Affairs: (412) 494-8000

d. *Synonym*: TD 2335

Mode of Action

Mussels do not sense this compound in the water and therefore do not close their shells; continued siphoning brings the material into contact with tissues where it acts as a corrosive to membranes, including gills.

It controls established populations of freshwater and saltwater mollusks, and prevents settlement of their immature forms. It also has activity against slime organisms in recirculating systems.

Toxicity is dependent on concentration and exposure time.

Application Strategies

Use this compound periodically for control of established populations in recirculating and once-through cooling water systems. It can be metered directly into the system.

It has potential for treating service water, auxiliary water, wastewater, influent, and fire protection water systems.

Timing of Application

Use when established populations are present.

During breeding and settling season, it can be used to prevent settlement of immature forms of mollusks.

Application Rates and Duration

For established populations in recirculating and once-through cooling water systems, apply at 0.3 to 3.0 ppm of the active ingredient endothall for 6 to 144 hr of exposure. These concentrations are equivalent to 9.1 to 91 L per 38,000,000 L water (2.4 to 24 gal of EVAC per 1,000,000 gal of water).

The higher rates of application and exposure times are required for heavy populations of fouling mollusks and/or with cooler water temperatures (less than 70 EF or 21 EC).

Laboratory studies show that efficacy is dependent on rate of application and time of exposure. For example, treatments of 2.3 ppm for 6 to 7 hr were equivalent to those at 5 ppm for 2 hr.

For byssal thread detachment, use 0.5 mg L^{-1} (Piccirillo, Dionne, and Sandberg 1997).

Posttreatment and Discharge

EVAC does not require a holding period or deactivation after use.

Discharge limits are approximately 50 ppb of amine.

EVAC rapidly dissipates in water. Degradation in the environment is microbial only; it does not hydrolyze or photolyze in an aquatic environment.

Use Restrictions

EVAC can be toxic to fish. Do not discharge effluent containing EVAC into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System permit and notification of the permitting authority in writing prior to discharge.

Do not discharge effluent containing EVAC into sewage systems without previously notifying the local sewage treatment authority. For guidance contact the State Water Board or Regional Office of the U.S. Environmental Protection Agency.

Timing of Effects

Treatment effects are evident within a few days of treatment. Maintain treatment through season.

Toxicological Data

The Signal Word/Toxicity Class is Danger.

This pesticide is toxic to fish.

It is nonpersistent and rapidly degraded by microbes to carbon, hydrogen, and oxygen (Simsiman 1976). It has short persistence and does not bioaccumulate, does not form toxic metabolites, or require detoxification. It has low to intermediate nontarget toxicity at regular application rates, as listed in the following tabulation.

Toxicity of Dimethylalkylamine Endothall

Species	Conditions	Exposure Period, hr	Acute Toxicity, Median Lethal Concentration, mg L^{-1}
Largemouth bass	Static	96	0.1-0.3[1]
Bluegill sunfish	Static	48	0.8
		96	0.06-0.2[1]
Redear sunfish	Static	96	0.1-0.2[1]
Golden shiner	Flow-through	120	0.32-1.6

Note: Data from Calgon Corporation (1998a).
[1] Diamine salt.

Precautions

EVAC is a concentrated product. It is fatal if absorbed through skin, and may be fatal if swallowed or inhaled.

It is corrosive, causing irreversible eye damage and skin burns. Do not get in eyes, on skin, or on clothing.

Wear the following personal protective equipment for concentrated product: coveralls over long-sleeved shirt and long pants; waterproof gloves; protective eyewear; chemical-resistant footwear plus socks.

Field Instructions and Guidance on Operational Applications

Suspension of the blowdown from cooling towers for 6-12 hr after application and/or segmenting plantwide treatments will reduce the level of product remaining in the effluent.

This product appears to be most effective at temperatures greater than 63 EF (17 EC). At temperatures of between 63 and 54 EF (17 and 12 EC), the mortality of zebra mussels exposed to 3.0 mg L^{-1} (3 ppm) for 8 hr was approximately 20 percent compared with 80 percent mortality among zebra mussels exposed under the same conditions, but at a temperature of 68 EF (20 EC) (Piccirillo, Dionne, and Sandberg 1997).

Adjuvant or Deactivant Use

No deactivant is required.

Application Techniques

EVAC can be metered directly into the system with a positive displacement pump or into a flow of dilution water for use in a distribution header. One continuous application should be made at a convenient point of uniform mixing, such as a basin area, pump area, or other reservoir or collecting area from which treated water will be circulated uniformly throughout the system.

Antidote Information

Use the following antidotes:

a. *If swallowed*: call a physician or Poison Control Center. Have the victim drink 1 or 2 glasses of water and induce vomiting, unless person is unconscious.

b. *If on skin*: wash with plenty of soap and water. Get medical attention.

c. *If in eyes*: hold eyelids open and flush with water for 15 min. Get medical attention.

d. If inhaled: remove victim to fresh air. Get medical attention.

e. Note to physician: probable mucosal damage may contraindicate use of gastric lavage. Measures against circulatory shock, respiratory depression, and convulsion may be needed.

f. Emergency phone number:

(1) Calgon Corporation: (412) 494-8000

(2) CHEMTREC: 1-800-424-9300

References

Calgon Corporation. (1998a). "EVAC™ Biocide. Material Safety Data Sheet," Pittsburgh, PA.

Calgon Corporation. (1998b). "EVAC™ Biocide. Registered label," Pittsburgh, PA.

Piccirillo, V. J., Dionne, E., and Sandberg, G. (1997). "TD 2335: Laboratory and field efficacy studies for control of zebra mussels in electric power plants," *Zebra mussel and aquatic nuisance species*. F. M. D'Itri, ed., Ann Arbor Press, Chelsea, MI, 534-540.

Simsiman, G. V. (1976). "Diquat and endothall: Their fates in the environment," *Residue Reviews* 62, 131-74.

Metals and Their Salts

Both copper and a range of potassium salts have been shown to have activity against zebra mussels. Their low toxicity to other organisms in water and long history of use in water treatment make them potential solutions for a range of problem zebra mussel sites and systems.

Copper Ions

The presence of excess copper ions in water is inimical to a number of aquatic organisms, including algae, plants, mussels and clams, and has a long history of use in marine antifouling coatings. McMahon and Tsou (1990) note that copper is relatively lethal to zebra mussels, with 5 ppm copper ions for 24 hr giving 100 percent kill of veligers.

MacroTech

The commercial MacroTech ZM-Series devices employ copper and aluminum anodes to supply copper ions to water at a low but toxic level. The gelatinous nature of the aluminum hydroxide formed enhances flocculation and deposition of the copper ion on surfaces, which then makes them unacceptable for settling (Blume, Fraleigh, and Van Cott 1994; Race 1995; Blume and Fitzgerald 1996).

Chemical Name and Commercial Formulations

The MacroTech technique uses these compounds:

a. Chemical:

- Copper ions (Cu^{++}) and Aluminum (Al)
- Aluminum hydroxide ($Al(OH)^{3}$)

b. *Source*: MacroTech, Inc.
246 Mamaroneck Road
Scarsdale, NY 10583-7242
(914) 723-6185
wjblume@prodigy.net

Mode of Action

Incoming water is treated with copper and aluminum by the controlled electrolytic dissolution of anodes of these materials to produce copper ions and aluminum hydroxide. Presence of copper in water inhibits veliger activity and development through direct toxicity. The aluminum hydroxide has a flocculent activity that aids in precipitating veligers, and it forms an anodic, fluid film on surfaces, which acts as an antifouling coating to inhibit biofilm formation and postveliger settlement. This activity also reduces potential for microbiologically induced corrosion.

Application Strategies

Deploy this device to treat incoming water in flow-through or recirculating service water systems.

Timing of Application

To prevent settlement at the postveliger stage, apply on a continuous basis during the reproductive and settling season.

Application Rates

The MacroTech unit maintains copper ions at 5 to 10 ppb above ambient levels.

Maximum Water Concentration

Currently the U.S. Environmental Protection Agency Drinking Water Standard for copper is a maximum contaminant level of 1.3 mg L^{-1} or 1,300 ppb (U.S. Environmental Protection Agency 1991).

No detoxification is required. Water can be discharged to potable water without detoxification.

Use Restrictions

Copper concentration should not exceed 1 mg L^{-1} (potable water) by weight copper.

Currently, there are no restrictions on the use of treated water immediately following treatment.

Timing and Appearance of Effects

Copper is relatively lethal to zebra mussel; 5 ppm Cu for 24 hr has been shown to give 100 percent kill (McMahon and Tsou 1990).

Toxicological Data

The Signal Word is Caution.

Copper toxicity to aquatic organisms can vary with water hardness, as shown in the following tabulation.

Toxicity of Copper to Aquatic Organisms				
Species	**Chemical**	**Hardness mg L^{-1} as $CaCO_3$**	**Exposure Period, hr**	**Acute Toxicity, Median Lethal Concentration, mg L^{-1}**
Cutthroat trout	Copper chloride	18-205	96	15.7-367
Rainbow trout	Copper chloride	42-194	96	57-574
White perch	Copper nitrate	53	96	6,200
Striped bass	Copper nitrate	53-55	96	4,000-4,300
Bluegill sunfish	Copper chloride	43	96	1,250
Largemouth bass	Copper nitrate	100	96	6,970

Precautions

Monitor water hardness and presence of desirable aquatic species in outfall water.

Exposure to copper may produce skin and gastrointestinal irritation.

Field Instructions and Guidance on Operational Applications

Install MacroTech treatment unit as directed by manufacturer.

Adjuvant/Detoxicant/Deactivant Use

None is required.

Application Techniques

A side stream of fresh water is passed through the MacroTech treatment unit, wherein a copper and aluminum concentrate is formed. The treated water is then reinjected to the intake for final dilution and the treatment of the entire system.

Antidote Information

Wash contacted areas. Get medical attention if irritation persists.

References

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Potassium Compounds

The K^+ ions of potassium compounds have some selective activity, being highly toxic to zebra mussels, where they interfere with membrane integrity and respiration (Fisher et al. 1991; Claudi and Mackie 1994), but not affecting fish (Waller et al. 1993). While too harmful to native mussels to have gained approval for use in once-through systems, potassium is suitable for contained or closed-loop systems, or those such as fire protection systems where outfall of large amounts of concentrated solutions is not a problem (Claudi and Mackie 1994; Lewis et al. 1996). A method for treating such semistatic systems with the effects of potassium ions (K+), using commercially available potash has been developed by Aquatic Sciences, Inc., Canada. As an unregulated, low-cost product, potash has been shown to be acutely toxic to mussels under both warmwater and coldwater conditions (>5 ºC). At relatively low levels, potassium also appears to be a selective molluscicide. Since potash is regularly used as a fertilizer in agriculture, it is widely available and generally regarded as safe.

Chemical Name and Commercial Formulations

Potassium is available from various sources under the following chemical names:

a. Potassium phosphate, monobasic, KH_2PO_4

b. Potassium chloride, KCl

c. Potash

Mode of Action

Potassium causes several changes in zebra mussels, including prevention of valve closure, reduction in filtration rate, and mortality (Wildridge et al. 1996). It is thought to kill adult mussels by destroying the membrane integrity of the gill epithelium, thus eliminating the ability to respire (Fisher et al. 1991).

Application Strategies

Deliver a potassium-rich solution to water to be treated.

Timing of Application

Treatment can be at any time of year, as potash has been found to be efficacious at temperatures as low as 5 ºC (40 ºF).

Application Rates

Tests of various potassium salts show that adults are killed rapidly, with median lethal concentrations LC_{50}'s at 80 to 313 mg L^{-1} (Fisher et al. 1991). A concentration of 50 mg L^{-1} prevents settlement (Fisher, Fisher, and Polizotto 1993). The following tabulation lists the toxicities of potassium salts.

Toxicity of Potassium Salts to Zebra Mussel		
Potassium Salt	**LC_{50}, mg L^{-1}**	**Reference**
KCl	150 (48-hr) 138	Waller et al. 1993 Fisher et al. 1991
KH_2PO_4	92	Fisher et al. 1991
$K_4P_2O_7$ (potassium pyrophosphate)	94	Fisher et al. 1991

To prevent primary settlement, use 30 ppm on a continuous basis.

At water temperatures above 15 ºC, 40 ppm for 2 weeks gives control.

At water temperatures above 15 ºC, 100 ppm gives 100 percent mortality in 48 hr.

Maximum Water Concentration

Check with State agencies to see if a National Pollutant Discharge Elimination System permit is required for facility-specific discharge.

Use Restrictions

Restrict concentrations to maintain permitted discharge limits.

Timing and Appearance of Effects

Treatment effects are seen within 24 hours. Maintain treatment for effective control.

Toxicological Data

The following tabulation lists toxicities of potassium chloride.

Toxicity of KCl to Aquatic Organisms		
Organism	**Condition**	**No-Observed-Effect Level, mg L^{-1}**
Daphnia magna		>100
Gambusia affinis		>186
Helisoma spp.		>186
Anondonta imbecillus	With sediment Without sediment	>100 LC_{50} 76
Ceriodaphnia dubia		>100
Fathead minnows		>100
Rainbow trout		>100
Note: Data from Fisher et al. 1991.		

Precautions

These compounds may cause irritation during use. Avoid contact with eyes, skin, clothing, and wash them thoroughly after handling.

Field Instructions and Guidance on Operational Applications

Use biobox monitors to assess effectiveness of treatment.

Discharge to ground or to greater volumes of water.

Adjuvant or Detoxicant Use

No adjuvant or detoxification is required.

Application Techniques

Meter solution into water system.

Antidote Information

Use the following antidotes:

a. *Ingestion*: if swallowed and the person is conscious, immediately give large amounts of water. Get medical attention.

b. *Inhalation*: if a person breathes in large amounts, move the exposed person to fresh air. Get medical attention.

c. Eye contact: immediately flush with plenty of water for at least 15 minutes. Get medical attention.

d. Skin contact: immediately wash with plenty of soap and water for at least 15 minutes.

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Control and prevention of macrofouling caused by the freshwater zebra mussel, *Dreissena polymorpha* (Pallas), is a major concern of managers of inland waterways, water treatment plants, and power generation facilities in many areas of eastern North America. The threat to structures in navigable waterways makes the issue of interest to the U.S. Army Corps of Engineers.

In North America, chemical applications to water have been the most commonly used method of zebra mussel treatment and control for internal and closed systems. Numerous organic and inorganic chemicals with toxicity to zebra mussels can provide versatile, cost-effective, and easy to implement ways to deal with established populations, and can prevent new infestations. Chemical treatments can be designed to protect whole systems very safely when use and discharge are carried out in compliance with environmental regulations.

This report describes basic guidelines for the use of molluscicidal compounds that are currently registered with the U.S. Environmental Protection Agency for zebra mussel control.

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